United States Court of Appeals

for the

District of Columbia Circuit

TRANSCRIPT OF RECORD

FOR MR. JUSTICE ROBB

146
19

TRANSCRIPT OF RECORD

Court of Appeals of the District of Columbia

APRIL TERM, 1932

No. 5762

246

HENRY L. DOHERTY, APPELLANT,

vs.

THOMAS E. ROBERTSON, COMMISSIONER OF PATENTS.

APPEAL FROM THE SUPREME COURT OF THE DISTRICT OF COLUMBIA.

FILED AUGUST 9, 1932.

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Apr. 10, 19

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Court of Appeals of the District of Columbia

No. 5762.

HENRY L. DOHERTY, Appellant,
vs.
THOMAS E. ROBERTSON, Commissioner of Patents.

---

a Supreme Court of the District of Columbia.

In Equity.

No. 51214.

HENRY L. DOHERTY, Plaintiff,
vs.
THOMAS E. ROBERTSON, Commissioner of Patents,
Defendant.

UNITED STATES OF AMERICA,
District of Columbia, ss:

Be it remembered, That in the Supreme Court of the District of Columbia, at the City of Washington, in said District, at the times hereinafter mentioned, the following papers were filed and proceedings had in the above-entitled cause, to wit:

1 *Bill.*

Filed March 31, 1930.

In the Supreme Court of the District of Columbia.

In Equity.

No. 51214.

HENRY L. DOHERTY, Plaintiff,
vs.
THOMAS E. ROBERTSON, Commissioner of Patents,
Defendant.

The Plaintiff states as follows:

1. The Plaintiff, Henry L. Doherty, is a citizen of the United States and a resident of New York City, in the

County of New York and State of New York and brings this suit in his own right.

2. The defendant, Thomas E. Robertson, is the Commissioner of Patents of the United States, a legal resident of the District of Columbia and is sued as Commissioner of Patents of the United States.

3. This bill is filed in accordance with the provisions of the Federal laws of the United States as provided for under the Revised Statute 4915.

4. The Plaintiff, Henry L. Doherty, filed an application for a patent in the United States Patent Office entitled Method of Recovering Oil from Oil Sands on February 12, 1927 which was given the Serial Number 167,865.

5. The said application was filed in accordance with the laws of the United States and the Rules of the Patent Office.

6. The said application has been duly prosecuted in accordance with the laws of the United States and the Rules of the Patent Office.

7. The said application has been acted upon by the Primary Examiner who refused to allow the following claims:

2 1. A method of obtaining oil from oil fields comprising forcing a liquefied mixture of butane and propane saturated with hydrocarbon gas into an oil stratum, and recovering oil from the stratum at a point remote from the point of introduction of the mixture into the stratum.

2. A method of obtaining oil from oil fields comprising forcing a liquefied mixture of butane and propane saturated with hydrocarbon gas under high pressure into an oil stratum under a relatively lower pressure, and recovering oil from the stratum at a point removed from the point of introduction of the mixture into the stratum.

3. A method of obtaining oil from oil fields comprising forcing a liquefied mixture of butane and propane saturated with hydrocarbon gas under high pressure into an oil stratum, and recovering oil from the stratum at a point of relatively low pressure.

4. A method of obtaining oil from oil fields comprising forcing a liquefied hydrocarbon substance consisting of butane and propane with gas in solution under high pressure into an oil stratum and withdrawing oil from the stratum at a point of relatively low pressure.

5. A method of obtaining oil from oil fields comprising forcing a mixture of hydrocarbon constituents having a molecular structure including less than six carbon atoms into an oil stratum and recovering oil from the stratum.

6. A method of obtaining oil from oil fields comprising forcing a liquefied mixture of hydrocarbon constituents having a molecular structure including less than six carbon atoms into an oil stratum and recovering oil from the stratum.

7. A method of obtaining oil from oil fields comprising forcing a gas-saturated liquefied mixture of hydrocarbon constituents having a molecular structure including less than six carbon atoms into an oil stratum and recovering oil from the stratum.

8. A method of obtaining oil from oil sands comprising introducing into the stratum in the earth containing oil a liquid hydrocarbon mixture having a gravity viscosity and surface tension lower than gasoline and withdrawing oil and the liquid mixture from a portion of the stratum different from that in which the liquid mixture is introduced.

9. A method of obtaining oil from oil fields comprising introducing under pressure into the stratum containing the oil a hydrocarbon liquid which contains more than 100 volumes of gas in solution per volume of liquid, driving the liquid mixture, gas and oil through the sands to an outlet and withdrawing the mixture of oil, gas and liquid mixture through a well different from that in which the liquid mixture and gas are inserted into that stratum.

10. A method of obtaining oil from oil fields comprising forcing under pressure a mixture of hydrocarbon constituents having a molecular structure each less than six carbon atoms and containing many times its volume of gas in solution into one portion of a sand stratum containing oil
3 and recovering oil, hydrocarbon liquid and gas from
the oil stratum at a point removed from the point of introduction of the mixture and gas into the stratum, said point being of relatively lower pressure than the point of introduction of the mixture into that stratum.

11. The process of recovering oil from oil-bearing strata consisting in subjecting the oil-bearing strata to the action of a hydrocarbon gas saturated liquid propane-butane mixture introduced under pressure into the strata whereby the

oil in the strata is subjected to the motivating action of both liquid and gas.

Which he finally rejected in accordance with the Rules of the United States Patent Office.

8. The applicant appealed from the decision of the Primary Examiner to the Board of Appeals who affirmed the rejection of the Primary Examiner in their decision dated October 3, 1929.

9. The Commissioner of Patents by the Board of Appeals contends that the method for conserving natural gas and oil which is shown in the reference Wright, United States patent 1,101,605 dated June 30th, 1914, patentably anticipates the method of recovering oil from oil sands called for by the applicant's claims, and that there is no invention defined in applicant's claims over the disclosure of the said Wright patent.

10. The applicant disagrees with these contentions of the Commissioner of Patents and contends that the method for conserving natural gas and oil which is shown in the reference is not readable on, nor does it patentably anticipate, the method for recovering oil from oil sands which is called for by the claims, and that there is an invention in recovering oil from oil sands in the manner specified by each of the claims.

11. The Plaintiff further states that the said invention is new and useful and was not known or used by others in this country before his invention thereof and not patented or described in any printed publication in this or any foreign country before his invention thereof, or more than
4 two years before his application for patent therefor,
and not in public use or on sale in this country for more than two years before his application and not patented in any country by him or his legal representatives on an application filed more than twelve months prior to his application for United States patent, and not abandoned.

12. The jurisdiction of this court depends upon the patent laws of the United States, this being a suit in equity under Section 4915, Revised Statutes (Comp. Stats. 9460; U. S. C. Title 35, Section 63), as amended by act of March 2, 1927, to secure an adjudication that plaintiffs are entitled to receive a patent for the invention as specified in

the rejected claims hereinafter referred to or for any part thereof, as the facts in the case may appear, and that the defendant be authorized to issue such patent.

Under the provision of said act of March 2, 1927, the said decision of the Board of Appeals of the Patent Office constitutes a refusal by the Commissioner of Patents to grant a patent on said invention as defined by said claims 1 to 11, inclusive, and no appeal has been taken from the decision of the Board of Appeals to the Court of Customs and Patent Appeals and no such appeal is pending or has been decided. Said decision of the Board of Appeals was delivered on or about October 3, 1929, and within the six months last past, and notwithstanding the said decision of the Board of Appeals, the plaintiff applicant is entitled to receive a patent for the improvement aforesaid constituting the subject-matter of said claims.

Wherefore the plaintiff prays the Honorable Court:

First, to adjudge and decree that the plaintiff is the true, first, original and sole inventor of the improvement set forth in the said claims 1 to 11, inclusive, hereinabove recited.

5 Second, to adjudge and decree that the plaintiff is entitled according to law to receive a patent for the invention specified in and covered by said claims 1 to 11, inclusive, or for any part thereof, as the facts in the case may appear.

Third, to authorize and direct the Commissioner of Patents to issue to plaintiff Letters Patent of the United States embodying said claims 1 to 11, inclusive, upon the filing in the Patent Office of such adjudication and upon compliance with the requirements of law in such cases made and provided.

Fourth, that the plaintiff have a writ of subpena ad respondendum of the United States of America directed to said Thomas E. Robertson, as Commissioner of Patents, commanding him on a day certain therein to be named to appear and answer to this bill of complaint, but not under oath, an answer under oath being expressly waived, and to abide by and perform all and singular such orders and decrees in the premises as to this court which seem proper and conformable to the principles of equity and good conscience; and that the plaintiff have such other and further relief as may be just and proper.

And your orators, as in duty bound, will ever pray.

HENRY L. DOHERTY,
Plaintiff.
EDMUND G. BORDEN,
Counsel for Plaintiff.
J. AUSTIN STONE,
Associate Counsel for Plaintiff.

COUNTY OF NEW YORK,
State of New York, ss:

On this 24th day of March, 1930, personally appeared before me the above-named Henry L. Doherty, the Plaintiff named in the foregoing bill and being duly sworn did depose and say that he has read the foregoing bill and that the same is true to the best of his knowledge and belief.

[SEAL.]
THOMAS H. FAIR,
Notary Public, Kings County.

Commission expires March 30, 1932.

Answer to Bill.

Filed April 18, 1930.

* * * * * * *

To the Honorable the Judges of the Supreme Court of the District of Columbia:

1. Defendant answering the Bill of Complaint admits for the purpose of this suit the allegations of paragraph 1.
2. Defendant admits that as Commissioner of Patents his official residence is in the District of Columbia and that his legal residence is in Chevy Chase, Maryland.
3. Defendant admits that this Court has jurisdiction under Section 4915 R. S. (35 U. S. C. A. 63).
4. Defendant admits that plaintiff, on February 12, 1927, filed an application for patent in the United States Patent Office, to which was given Serial No. 167,865.
5. Defendant admits the allegations of paragraph 5.
6. Defendant admits that the said application was duly prosecuted in accordance with the laws of the United States and the Rules of the Patent Office.
7. Defendant admits that the examiner acted upon the application and refused to allow the claims recited in para-

graph 7, which claims were finally rejected in accordance with the Rules of the Patent Office.

8. Defendant admits that the applicant appealed
7 from the decision of the primary examiner to the
Board of Appeals, who affirmed the decision of the
primary examiner.

9. Defendant admits the allegation of paragraph 9.

10. Defendant admits that plaintiff contends that the said claims are patentable but defendant denies that the claims are patentable to plaintiff in view of the patent to Wright, 1,101,605, dated June 30, 1914, and the disclosure on pages 438 to 440, inclusive, of the book entitled "The American Petroleum Industry", Volume 1, by Bacon and Hamor, published by McGraw-Hill Book Company, Inc., 239 West 39th St., New York, N. Y., as more fully appears from the statement of the Examiner and the decision of the Board of Appeals. Profert of copies is hereby made.

11. Defendant admits that plaintiff in his said application, Serial No. 167,865, made the averments specified in paragraph 11, but defendant has no knowledge thereof except as informed by the Bill.

12. Defendant admits the allegations of paragraph 12, except the allegation that plaintiff is entitled to receive a patent for the subject matter of the said claims.

Further answering, defendant denies that the claims recited in paragraph 7 are patentable to plaintiff in view of the patent to Wright and the publication.

And further answering, defendant denies each and every allegation of the Bill of Complaint not herein specifically and sufficiently denied or admitted, and prays that plaintiff's Bill of Complaint be dismissed.

Wherefore defendant having fully answered the Bill of
Complaint denies that plaintiff is entitled to the relief de-
manded or any part thereof and prays that he be hence
dismissed with all costs and expenses of the pro-
8 ceedings against the plaintiff as required by Section
4915 R. S.

THOMAS E. ROBERTSON,
Commissioner of Patents, Defendant.

T. A. HOSTETLER,
Solicitor of the U. S. Patent Office,
Attorney for Defendant.

District of Columbia,
City of Washington, ss:

I, Thomas E. Robertson, Commissioner of Patents, depose and say that I have read the above answer by me subscribed and know the contents thereof, and that the statements of facts therein made as upon personal knowledge are true, and those made upon information and belief I believe to be true.

THOMAS E. ROBERTSON,
Commissioner of Patents.

Subscribed and sworn to before me this 18th day of April, 1930.

[SEAL.] FANNIE W. SCHRIDER,
Notary Public, D. C.

My commission expires May 12, 1933.

Findings of Fact.

Sumbitted by Defendant.

Filed April 7, 1932.

* * * * * * *

1. Plaintiff's application discloses a method of recovering oil from a partially depleted oil sand body by forcing a gas saturated liquefied propane-butane hydrocarbon downwardly into a well, through the oil stratum where it dissolves in the oil reducing the viscosity and then
9 carrying the mixture to and out through another well.

2. The patent to Wright 1,101,605 discloses a method of recovering oil by forcing hydrocarbon gases (natural gas) under pressure into a well and through the oil bearing rock where it extracts oil, and then carrying the mingled gas and oil to and out through another well. The hydrocarbon gases are first liquefied by pressure and a cooling b-ine.

3. The hydrocarbons utilized principally by plaintiff are gaseous at normal temperature and pressure. Plaintiff liquefies the butane and propane and saturates the thus liquefied propane and butane with gaseous methane and ethane. All of these gaseous hydrocarbons are present in substantial amounts in natural gas.

Conclusions of Law.

1. The claims do not patentably distinguish from the prior art adduced by defendant.

2. The Wright patent 1,101,605 having disclosed the process of extracting oil from oil-bearing rock by means of natural gas (hydro-carbon) liquefied by cooling and pressure, plaintiff did not invent a new process by merely utilizing in that process a hydrocarbon mixture consisting principally of butane and propane together with other hydrocarbon ingredients.

3. Plaintiff is not entitled to a decree for the claims and the Bill of Complaint will be dismissed.

DANIEL W. O'DONOGHUE,
Justice.

April 7th, 1932.

Final Decree.

Filed April 7, 1932.

* * * * * * *

This cause having come on to be heard and having been tried in open court and argued by counsel for the respective parties upon the pleadings and proofs adduced and submitted to the Court,

It is adjudged, ordered, and decreed that the Bill of Complaint in this case be, and the same hereby is dismissed.

DANIEL W. O'DONOGHUE,
Justice.

April 7th, 1932.

Approved as to form:
J. AUSTIN STONE,
Attorney for Plaintiff.

Petition of Appeal.

Filed April 30, 1932.

* * * * * * *

The plaintiff, Henry L. Doherty, conceiving himself aggrieved by the final decree made and entered herein on or about April 7, 1932, does hereby appeal from the said de-

cree to the Court of Appeals for the District of Columbia, for the reasons specified in the Assignment of Errors, which is filed herein; and he prays that this appeal may be allowed and a citation granted directed to the above named Thomas E. Robertson, Commissioner of Patents, commanding him to appear before the Court of Appeals of the District of Columbia, to do and receive what may appertain to justice to be done in the premises, and that a transcript of the record, proceedings and papers upon which said decree was made, be duly authenticated, and, together with
11 all models and exhibits filed in said cause, to be filed with the Clerk of the Court of Appeals for the District of Columbia.

J. AUSTIN STONE,
Attorney for Plaintiff.

April 29, 1932.

Order Allowing Appeal, &c.

Filed April 30, 1932.

* * * * * * *

The plaintiff, Henry L. Doherty, having filed his petition for appeal from the final decree made and entered herein on or about the 7th day of April, 1932, it is

Ordered that the said appeal of said plaintiff, Henry L. Doherty, from said decree to the Court of Appeals of the District of Columbia be, and the same is hereby allowed.

Ordered further that the amount of security of the costs which the plaintiff shall give on said appeal be, and the same is hereby fixed at the sum of one hundred dollars.

And it is further ordered that upon the giving of such bond, a certified transcript of the records, proceedings and papers herein, together with all models and exhibits be forthwith transmitted to the said Court of Appeals of the District of Columbia.

Dated this 29th day of April, 1932.

JESSE C. ADKINS,
Justice.

Service of the within Order allowing appeal of plaintiff from final decree admitted this 29th day of April, 1932.

T. A. HOSTETLER,
Solicitor for Defendant.

12 *Order Allowing Appeal, &c.*

Filed April 30, 1932.

* * * * * * *

The plaintiff, Henry L. Doherty, having filed his petition for appeal from the final decree made and entered herein on or about the 7th day of April, 1932, it is

Ordered that the said appeal of said plaintiff, Henry L. Doherty, from said decree to the Court of Appeals of the District of Columbia be, and the same is hereby allowed.

Ordered further that the amount of security of the costs which the plaintiff shall give on said appeal be, and the same is hereby fixed at the sum of one hundred dollars, or in lieu thereof a deposit in cash in said amount.

And it is further ordered that upon the giving of such bond, a certified transcript of the records, proceedings and papers herein, together with all models and exhibits be forthwith transmitted to the said Court of Appeals of the District of Columbia.

Dated this 30th day of April, 1932.

PEYTON GORDON,
Justice.

Memorandum.

April 30, 1932.—$100 deposit in lieu of bond on appeal.

13 *Citation.*

Issued April 30, 1932.

* * * * * * *

The President of the United States of America to Thomas E. Robertson, Commissioner of Patents, Greeting:

You are hereby cited and admonished to be and appear at a Court of Appeals of the District of Columbia, upon the docketing the cause therein, under and as directed by the Rules of said Court, pursuant to an Appeal noted in the Supreme Court of the District of Columbia, on the 30″ day of April, 1932, wherein Henry L. Doherty is Appellant, and you are Appellee, to show cause, if any there be, why the Decree rendered against the said Appellant, should not be corrected, and why speedy justice should not be done to the parties in that behalf.

Witness the Honorable Alfred A. Wheat, Chief Justice of the Supreme Court of the District of Columbia, this 30″ day of April, in the year of our Lord one thousand nine hundred and thirty-two.

[SEAL.] FRANK E. CUNNINGHAM,
Clerk,
By HARRY M. HULL,
Assistant Clerk.

Service of the above Citation accepted this 30″ day of Apr., 1932.

T. A. HOSTETLER,
Attorney for Appellee.

14 *Assignment of Errors.*

Filed April 30, 1932.

* * * * * * *

Now comes Henry L. Doherty, the above named plaintiff by his attorney, J. Austin Stone, and having prayed an appeal to the Court of Appeals of the District of Columbia from the final decree and order made and entered in this cause on the 7th day of April, 1932, says that said decree and order are erroneous and unjust and against the rights of said plaintiff, and as Assignment of Errors therein represents that said Supreme Court of the District of Columbia erred in the following particulars:

1. In basing the decree on the statements embodied in the findings of fact and conclusions of law "submitted by defendant."
2. In failing to take cognizance of the points emphasized in the findings of fact and conclusions of law submitted by the plaintiff and supported by testimony for the plaintiff.
3. In finding the invention described and claimed in plaintiff's application for patent, Serial 167,865, not patentable in view of the disclosure in the United States patent to Wright, 1,101,605.
4. In finding that the plaintiff did not invent a new process by conducting the steps described and claimed in said application for patent as distinguished from the disclosure in the said patent to Wright.

5. In dismissing plaintiff's Bill and in not sustaining it.

Wherefore the plaintiff prays that the said decree be reversed and that the plaintiff be adjudged entitled to the requested patent.

J. AUSTIN STONE,
Attorney for Plaintiff.

15 *Memoranda.*

May 14, 1932.—Statement of evidence in duplicate filed.

June 14, 1932.—Statement of evidence signed (in duplicate).

Docket Entries.

* * * * * * *

Date.	Proceedings.
1930, Mar. 31.	Deposit for costs by Stone.
" " "	Bill, appearance, order to file, filed.
" " "	Spa. to answer & copy issued Ret'd 4/7/30 served.
" Apr. 18.	Answer of deft. to bill, App. Hostetler, filed.
" Nov. 7.	Calendared per order plff's atty., filed.
1932, Apr. 7.	Findings of Fact.
" " 7.	Final Decree Dismissing Cause.
" " 30.	Petition of plff. for appeal.
" " "	Order allowing appeal & fixing bond at $100, or $100 cash in lieu, filed.
" " "	Assignment of Errors filed.
" " "	Order extending time to file statement of Evidence to May 14, 1932, filed.
" " "	Additional deposit by Stone for appeal.
" " "	Citation on appeal. Service accepted.
" " "	Deposit by J. Austin Stone for plff. in lieu of bond on appeal.
" May 14.	Acknowledgment of Service filed.
" " "	Designation of Record filed.
" " "	Statement of Evidence in duplicate filed.
" June 14.	" " " Signed (in duplicate) filed.

16 *Designation of Record.*

Filed May 14, 1932.

* * * * * * *

Now comes Henry L. Doherty, the appellant in the above entitled cause, and designates the parts of the record which he desires to have included in the transcript, said parts being considered sufficient for the determination of the questions raised on appeal, namely:

1. Docket Entries.
2. Bill of Complaint.
3. Answer.
4. Statement of Evidence.
5. Copy of Findings of Fact and Conclusions of Law as adopted by the court.
6. Decree.
7. To be certified as physical exhibits: the various sand samples comprising Exhibit C.
8. The following exhibits:

Plaintiff's Exhibit “A”, i. e. certified copy of Doherty Application and claims including amendments.

From Plaintiff's Exhibit “D”, i. e. three articles by Uren in the National Petroleum News over the period January 26, 1927 to February 9, 1927, comprising pages 71 and 72 of the article in the January 26 number and pages 67, 68, 71-2-4-6 of the article in the February 9 number of National Petroleum news.

From Plaintiff's Exhibit F, i. e., the Beecher & Parkhurst article beginning on page 51 of the A. I. M. M. E. publication, “Petroleum Development and Technology”, 1926, comprising pages 51, 2, 4, 5, 6, 8, 9, and 63.

From Plaintiff's Exhibit “H”, Bureau of Mines R. I. 3035 by Chalmers et al., published September 1930, on “The Recovery of Oil from Sands by the Gas Drive”, comprising table 4 on page 5, curves comprising figures 2 and 3 on pages 6-A and 6-B and figure 5 on page 8-B, and tables 5 and 6 on pages 11 and 12.

From Plaintiff's Exhibit “I”, i. e. article by Ben E.
Lindsly, Engineer of the U. S. Bureau of Mines, “Oil
17 and Gas Journal” May 14, 1931, pages 92, 146, 148,
150, 152, 153, 154.

From Plaintiff's Exhibit “J”, i. e., the article by Per K. Frolich, et al., on “The Solubilities of Gases in Liquids at High Pressure”, published in Volume 23, No. 5 page 548 of Industrial & Engineering Chemistry, and pages 548, and Figs. 1 and 2.

From Plaintiff's Exhibit “K”, i. e., the article by Wm. M. Lacey, on “Experiments on Rates of Solution of Oil and

Gas'', published in A. P. I. Production Bulletin #2071 June 1931, pages 166, 167, 174 and 177.

From Plaintiff's Exhibit "N", certified file history of the Little patent 1,762,783, comprising the printed copy of the Little patent, and the following file references stipulated to be patents cited by the Patent Examiner against the patent: namely, Clope 1,112,359; Waller 922,369; Frankforter 918,990; Ogilvey 1,264,551; Yaryan 915,400.

9. Defendant's Exhibits:

Exhibit 1. Wright patent 1,101,605.

Exhibit 2. Pages 438, 439 and 440, inclusive, of American Petroleum Industry, by Bacon and Hamor. Vol. 2, 1916.

Exhibit 3. The Examiner's Statement from the Doherty file before the Board of Appeals.

Exhibit 4. The decision of the Board of Appeals on Doherty's Appeal.

10. Order approving Statement of Evidence.

11. Petition of Appeal and Order allowing same.

12. Assignments of Error.

13. Citation.

14. Copy of this Designation of the Record and Stipulation appended thereto.

15. Clerk's Certificate.

By J. AUSTIN STONE,
Of Counsel.

18 *Stipulation.*

It is this 14th day of May, 1932, hereby stipulated and agreed by and between the parties hereto, by their respective attorneys, that the transcript on appeal shall constitute those parts of the original proceedings as are set forth in the foregoing Designation of the Record, to which this Stipulation is appended.

It is further stipulated and agreed that the Statement of Evidence as prepared and filed by the plaintiff, service and receipt of a copy of which is acknowledged by the defendant, shall constitute the Statement of Evidence for the purpose of this appeal and that the same may be received without further amendment, defendant hereby consenting to the immediate approval of said Statement of Evidence by the court, and hereby waiving the period allowed under the rules in which to make objection and/or present amendments.

J. AUSTIN STONE,
Of Counsel for Plaintiff.
T. A. HOSTETLER,
Of Counsel for Defendant.

19 Supreme Court of the District of Columbia.

UNITED STATES OF AMERICA,
District of Columbia, ss:

I, Frank E. Cunningham, Clerk of the Supreme Court of the District of Columbia, hereby certify the foregoing pages, numbered from 1 to 18, both inclusive, to be a true and correct transcript of the record, according to directions of counsel herein filed, copy of which is made part of this transcript, in cause No. 51214 in Equity, wherein Henry L. Doherty is Plaintiff and Thomas E. Robertson, Commissioner of Patents, is Defendant, as the same remains upon the files and of record in said Court.

In testimony whereof I hereunto subscribe my name and affix the seal of said Court, at the City of Washington, in said District, this 5th day of August, 1932.

[Seal Supreme Court of the District of Columbia.]

FRANK E. CUNNINGHAM,
Clerk,
By CHAS. B. COFLIN,
Assistant Clerk.

20 In the Supreme Court of the District of Columbia.

In Equity.

51214.

HENRY L. DOHERTY, Plaintiff,

vs.

THOMAS E. ROBERTSON, Commissioner of Patents,
Defendant.

Statement of Evidence.

Be it remembered that the above-entitled cause came on for trial upon the issues framed by the pleadings on Thursday, February 25, 1932, Mr. Justice Daniel W. O'Donoghue, presiding.

Appearances:

On behalf of the United States: T. A. Hostetler, Esq.

On behalf of the Plaintiff: J. Austin Stone, Esq., Kenneth I. White, Esq.

Thereupon, the counsel for plaintiff, after making an introductory statement of the nature of the case, explained that the case was before the court in order to secure a decree instructing the Commissioner of Patents to issue a patent to the plaintiff on the application of Henry L. Doherty, the plaintiff in this case.

In opening the case, Counsel called the Court's attention to a large colored chart set up on an easel in view of the Court, illustrating the principle of application of the invention of the Doherty patent application in suit. Counsel stated the chief problem which the Doherty invention seeks to solve is that of increasing the recovery of oil from
21 underground oil-bearing sands, which by present methods of production recover only about fifteen to twenty-five per cent of the oil in the ground. Counsel continued with an explanation of the Doherty invention as illustrated by the drawing, stating that the invention consists of a process involving the steps of taking the waste by-product propane and butane gases from the natural gas gasoline recovery plant in a gaseous state, liquefying the propane and butane, passing the liquefied propane and butane through a gas saturating apparatus wherein the liquid is saturated with dry natural gas, and introducing the thus gas saturated liquid propane and butane into the oil sand through the well. Counsel went on to explain that the gas saturated liquid propane and butane goes into solution in the oil in the sand, acts as a solvent for removing the oil from the surface of the sand grains, carries into solution in the oil a gas with which the liquid propane — butane is saturated, and on going out of solution in the oil adjacent the producing well serves as a propelling medium for forcing the oil out through the producing wells.

Counsel further explained that the Patent Office had rejected the Doherty application chiefly on the disclosure of

the Wright patent reference 1,101,605. Counsel explained that the Wright patent disclosure contemplates passing natural gas down through one well into an oil-bearing sand, introducing refrigerated brine into the casing of the well through which the gas is passed into the sand for the stated purpose of liquefying whatever portion of the gas will liquefy the oil being removed from the sand through another well. Counsel's description of the Wright patent disclosure was also illustrated to the Court by a colored enlarged photoprint of the drawing of the Wright
22 patent disclosure.

After stating that the question at issue was whether Doherty's process involving the use of gas saturated liquid propane and butane represents a real patentable improvement over the disclosure of the Wright patent reference in view of the disclosure of pages 438 to 400 of the Bacon and Hamor text; and after pointing out that it is Doherty's contention that Wright's disclosed system of cooling would not be operative to liquefy propane and butane, Counsel called as the Plaintiff's witness, **Mr. Charles E. Beecher**, explaining that Mr. Beecher's testimony, taken as that of an expert engineer familiar with oil production problems, was deemed desirable, in view of the basing of the decision of the Defendant Patent Commissioner chiefly on the conclusions of the Patent Examiner as a so-called "expert" by reason of his familiarity with the literature, and not by reason of any practical knowledge of oil production practice.

Direct examination:

Mr. Beecher, after being first duly sworn as a witness, testifying in response to the queries by Counsel, stated as follows:

That his name is Charles E. Beecher, his age 42, his residence Bartlesville, Oklahoma, and his occupation that of Chief Oil Production Engineer for the Empire Companies. Witness stated that he was graduated from Stanford University in 1913 with the A. B. degree and 1914 with the advanced degree of Engineer.

To questions regarding his occupational experience, witness replied that he had worked as a construction engineer

for the California Highway Commission and later for
23 a contracting firm, having been engaged on the construction of refinery buildings and on a wireless station for the government in Seward, Alaska. That following that employment, he had served as a pilot in the Aviation Section of the United States Army, and in 1919 was employed as engineer on construction by the Union Oil Company of California. That for four years beginning in 1920 he had held various positions including research engineer and Assistant Chief Technologist, with the United States Bureau of Mines, during which period he wa*d* employed at Washington, D. C. and in Wyoming and Montana on various problems connected with the development, operation and production of oil on government reserves. Witness stated that following his Bureau of Mines employment he accepted a position with the Empire Company, Bartlesville, Oklahoma for the purpose of carrying on some research work for Henry L. Doherty in connection with the problem of increasing recovery of oil from sands, and that since that date he has been employed as Chief Oil Production Engineer for the Empire and affiliated companies.

To queries by Counsel regarding his experience with experimental and commercial solution of oil production problems, witness replied that he had carried on research work in this connection and also had direct charge of actual recovery problems for the Empire Companies for several years, both in new and partially depleted fields. Witness continued by stating that at Mr. Doherty's suggestion he had made a research investigation of the physical characteristics of oil as it exists underground, and of the changes in physical characteristics of the oil resulting from solution therein of natural gas under pressure. Witness
24 stated that his investigation had demonstrated that the surface tension and viscosity of the oil were materially changed due to the gas in solution and that his experiments indicated that gas was more soluble in the lighter hydrocarbons such as propane, butane and gasoline, than in the heavier hydrocarbons such as crude oil, under comparative conditions of pressure. Witness stated that the petroleum industry and producers had acknowledged his experimental results as authoritative and of value to the industry, citing as examples acknowledgments in published articles of Professor Lester C. Uren of the University

of California, and of Dr. Umpleby and others engaged in dealing with these problems; and that methods now in use for producing oil have been greatly changed due to the concepts developed as a result of these experiments. Witness identified a paper by Dr. J. B. Umpleby, acknowledging the value to the industry of Beecher's experiments, as to be published in the March, 1932 number of "Mining and Metallurgy" a magazine of the American Institute of Mining and Metallurgical Engineers, on "Changing Concepts in the Petroleum Industry." Witness also identified a series of articles of Professor Uren acknowledging witness's experiments, as being published in the National Petroleum News during the period January 19 to February 9, 1927.

At this point the following exhibits were proffered by Plaintiff's Counsel and accepted in evidence:

Exhibit A.—Certified copy of complete file wrapper of Doherty Patent Application Ser. No. 167,865.
" A′.—Condensed certified copy of Doherty Application as amended.
" B.—Certified copy of the completed file of the Wright patent Ser. No. 1,101,605.

25 To queries of Counsel concerning the factors affecting the recovery of petroleum from underground structures, Witness replied that these factors were primarily viscosity and surface tension of the oil, the porosity of the sand, the nature of the porosity, the nature of the sand grains; and the pressure within the reservoir. As illustrating the factor of surface tension, Witness cited the manner in which coffee rises into a lump of sugar dipped therein, and pointed out that the openings in the average oil sand are smaller than those in the lump of sugar, and that the power of the oil sand to retain oil because of the surface tension effect is a very important factor influencing oil recovery, especially from semi-exhausted fields. Witness then produced and discussed several samples of oil sand taken from various wells—one from the Mary Sudick well in the Oklahoma City field, one a sample of the Bartlesville sand, one a sand sample showing how the oil is still retained in the sand, which witness stated could not be removed from the sample except by some process which

would dissolve the oil. Witness stated that the samples were actual cores taken from the producing wells, that the Mary Sudick well is better than 6,000 ft. deep, the Bartlesville sand about 2,000 ft. and the Burgess sand about 1,500 ft. deep. Witness pointed out (transcript p. 11) that the oil must be pretty thin in order to flow at the rate of 20,000 to 40,000 barrels per day through sand of such fine porosity.

At this point Counsel offered the sand samples produced by the witness as Plaintiff's Exhibit "C".

Queried further by Counsel concerning the factors affecting the recovery of oil through wells, particularly with relation to the effect of dissolved gas in the propulsion of the oil, witness replied that movement of oil 26 through the sand was caused by the energy supplied by the compressed gas and the gas dissolved in the oil. Continuing his discussion, witness stated that petroleum as we see it at the surface cannot be moved through these sands except at tremendous pressure, and even then with a filtering effect; that when the oil is saturated with gas it becomes quite thin, so that even fairly viscous oils when saturated with gas at pressures of 500 to 1,000 lbs. or even 3,000 lbs., becomes almost as thin as kerosine. Continuing his explanation of the part played by free gas in moving the oil, witness stated that when a producing well is opened and the pressure thereby reduced on the sand, the gas comes out of solution in the oil and thereby supplies the energy for pushing the oil to the well, just as gas will come out of solution in soda water when the cork in the bottle is removed. Witness further stated that the solution of gas in the oil reduces the surface tension of the oil or, in other words, the ability of the oil to adhere and cling to the sand grains.

Answering queries of Counsel, witness stated that it was in connection with experiments conducted by him at Mr. Doherty's suggestion that he first obtained information concerning the physical properties of petroleum and the effect of dissolved gas therein. Witness stated that the results of his experiments were published in an article entitled, "Effect of Dissolved Gas Upon the Viscosity and Surface Tension of Crude Oil" by C. E. Beecher and I. P.

Parkhurst, in the Petroleum Division of the American Institute of Mining and Metallurgical Engineers.

Queried by the Court, witness stated that he was the author, that Henry L. Doherty is the head of the
27 Cities Service Company, that Henry L. Doherty
made the invention, that Witness did the mechanical work, that credit is given to Mr. Doherty in the first paragraph of the article, explaining why it was done and that it was done under his direction.

Queried by Counsel if he had any authority for his previous statement that the dissolved gas acts as a propelling medium for removing the oil, other than his own experience, Witness answered that it was a fact generally accepted by the industry as shown by experiments of others and written articles, that the dissolved gas has this propelling effect when pressure is released and the gas comes out of solution in the oil. For further explanation of this phase of the production problem, Witness cited the Bureau of Mines publication No. 2732 of December, 1926, by Dow & Calkin, entitled "Solubility and Effects of Natural Gas and Air on Crude Oil"; the paper by Mills and Heithecker on "Volumetric and Gravity Changes due to Solution of Gas in Crude Oil"; the paper by Chalmers and others on "The Recovery of Oil from Sands by the Gas Drive"; the paper by Ben E. Lindsly on "Solubility of Natural Gas in Crude Oil"; the paper by Per K. Frolich on "Solubility of Gas in Liquids at High Pressure" published in Industrial and Engineering Chemistry, Vol. 23 page 548; the paper by Wm. N. Lacey on "Experiments on the Rate of Solution of Oil and Gas", published in the A. P. I. Bulletin 207, June 1931—which was stated by the Witness to show very interesting figures on the rate at which gas will dissolve in oil, and on the effects on surface tension.

Witness testified that there had been papers published explaining the relative locations in which the propulsive force of the gas is released from the oil, including a
28 paper by Professor Lester C. Uren of the University
of California, published in the "National Petroleum News", February 9, 1927, beginning on page 67, and the recently published article by Uren in "Petroleum Technology in 1931" entitled, "Experimental Study of Pressure Conditions Within the Well Reservoir Rocks in the Vicinity of a High Pressure Producing Well". Witness stated that

Professor Uren shows very plainly that gases like propane and butane in solution in the oil come out of solution near a well where pressure is reduced, and that it is at that point that these gases do their work in bringing the oil into the well; that approximately fifty per cent of the energy of the gas in solution is used within a distance of 10 ft. of the well, the remainder of the energy of the gas being used in bringing the oil up to that point from a distance of say 300 ft. away from the well. Witness explained that the flow of oil might be considered as starting from the crust of a piece of pie and gradually increasing its rate of flow until a high velocity flow is reached at the apex of the pie where the well is located, and that it is within the last ten feet surrounding the well that such gases as propane and butane liberated from solution do the maximum amount of work in propelling the oil.

Counsel then offered in evidence as Exhibits the various papers and articles concerning which the witness had testified, identified by the witness as follows:

Exhibit D.—A series of three articles published by Professor Lester C. Uren in the National Petroleum News over the period January 19, 1927 to February 9, 1927.

Exhibit E.—Article by Professor L. C. Uren published in 1931 volume of American Institute of Mining and Metallurgical Engineers' "Petroleum Technology", entitled "Experimental Study of Pressure Conditions Within the Well Reservoir Rock in the Vicinity of a High Pressure Producing Well".

29 Exhibit F.—Article of Beecher and Parkhurst published in 1926 volume of American Institute of Mining and Metallurgical Engineers "Petroleum Development and Technology," pages 51 to 63.

Exhibit G.—Bureau of Mines publication No. 2893, October 1928, by Mills & Heithecker.

Exhibit H.—Bureau of Mines publication R. I. 3035, September 1930 by Chalmers et al.

Exhibit I.—Article of Ben E. Lindsly, published in 1931 number of "Petroleum Development and Technology", American Institute of Mining and Metallurgical Engineers, page 252; and also published in the "Oil and Gas Journal" of May 14, 1931.

Exhibit J.—Article published by Per K. Frolich et al. in Vol. 23, No. 5, page 548 of the May 1931 number of "Industrial and Engineering Chemistry".

Exhibit K.—Article by Wm. N. Lacey, published in American Petroleum Institute Bulletin No. 207 of June, 1931, page 166.

Exhibit L.—Bureau of Mines publication No. 2732, by Dow and Calkin.

Counsel explained that the articles put in evidence as exhibits were considered to outline the results of the latest experimental developments in oil production.

Replying to query by Counsel, witness stated that some recent experimental investigations of the production problem had been made under his direction, for the purpose of showing the solubility of different hydrocarbon diluents in crude oil, such diluents including the hydrocarbons butane and propane which are gaseous at normal temperature and pressure. Witness produced curves which he described as showing results of experimental work on the solubility of natural gas in Oklahoma City crude and as showing the relation between the viscosity of the oil and the per cent of hydrocarbon diluent. Witness cited the curves as showing that ten per cent of gasoline added to the oil reduced the viscosity approximately 26 per cent; ten per cent of butane added to the oil reduced the viscosity approximately 47½ per cent; and 10 per cent of propane added to the oil reduced the viscosity approximately 55 per cent. Witness cited the curves as emphasizing the large reduction of viscosity that can be expected from adding small quantities of propane and butane to the oil. Witness produced another curve as illustrating how the viscosity of heavier seaside crude oil of around 30° gravity is reduced much more for the same amount of propane and butane or natural gas in solution therein than is a lighter oil such as Oklahoma City crude of about 40° gravity.

Counsel then offered in evidence as Plaintiff's Exhibit "M" the curves concerning which the witness had just testified.

To query concerning the bearing of the results of his own investigations and those of other investigations mentioned by the witness on the invention of the Doherty application, Witness stated that the results of these investigations show very plainly that it is possible to deliver to the oil sand large quantities of energy in the form of gas dissolved in propane and butane; that propane and butane have a selective solubility for these gases and are also selective solvents for the oil, i. e., that propane and butane, dissolve oil much more readily than gasoline even. Witness cited the experiments described by Frolich et al. as corroborating the fact that methane is very highly soluble in propane and butane. Witness also cited the Dow and Calkins publication of the Bureau of Mines as describing experiments corroborating and acknowledging his own experiments.

Queried by the Court, witness said that there is no chemical change when the hydrocarbons are introduced
31 into the oil, but that the change is a physical one,
without chemical reaction. Witness stated that propane and butane were not new, had been previously used in chemistry and industry, and that they are just light hydrocarbon gases. Witness went on to state that methane is one of the lightest of hydrocarbon gases having the chemical structure CH_4, and that heavier hydrocarbons have more carbon and more hydrogen.

In reply to a query by the Court as to whether he claimed that there is any discovery in the fact of injecting a lighter gas into an oil, witness answered "No, the injecting of gas into the sand has been done for a number of years". Witness continued by stating that propane and butane when they are saturated with gases are carriers of energy and when in a liquid form, dissolve the oil, being good solvents, and by carrying gas with them in solution are even better solvents and will furnish energy for removing the oil. Witness agreed to the Court's query that they have been injecting gases for years in this industry, and in reply to the Court's query as to whether it was not a matter of almost common sense that hydrocarbon gas makes oil lighter, witness went on to explain that gas will not dissolve in oil readily by simply forcing gas into a well leading to the oil, that it actually takes agitation and movement to effect such solution but that *liquid* propane and butane added to the oil will mix and dissolve therein and wash off the oil film.

The Court then directed a query to Mr. Hostetler, Counsel for Defendant, as to whether the Wright patent did not have in mind that the gas would become liquefied, to which the reply was in the affirmative.

In reply to queries from the Court as to whether
32 the Wright patent process liquefied the gas before it
went down into the oil, witness replied that the gasoline hydrocarbons that would liquefy are comparatively few, and that the brine cooling arrangement proposed in the Wright patent is from a practical standpoint inoperative. Witness stated that propane and butane are produced in greater quantity than gasoline as byproducts in the manufacture of natural gas gasoline, that propane and butane are not desirable products to have in gasoline because they are too volatile, and that they are removed during the manufacture of gasoline by a stabilizing process. Witness stated that propane and butane thus obtained as a byproduct is normally wasted, except as it is used for special fuels, and that Mr. Doherty's idea is to take these large quantities of propane and butane, liquefy them, saturate them with gas, and pump them into the oil sands in liquid form, thus introducing a dissolving agent as well as a source of energy. Witness answered in the affirmative the Court's inquiry as to whether natural gas has some propane and butane in it, and went on to explain that when natural gas is produced from an oil field, a gasoline plant is set up in the field, which takes all the gas that can be obtained from the field; that this gas is processed and the gasoline is recovered; and that the residue gas left over from the natural gas gasoline recovery treatment may be used for operating gas engines and the residue burned in a torch—i. e., wasted. Mr. Doherty's idea, as stated by the Witness, is to take this waste propane and butane, compress and liquefy it and saturate it with gas and put it back into the well. Witness stated that large quantities of propane and butane had been recently pumped in a
liquid state into the Burbank field in Oklahoma, as
33 much as 100,000 gallons a day, without saturating
with gas as proposed by Mr. Doherty. Witness said
that liquid propane and butane thus introduced into the

Burbank field had had quite a beneficial effect on the recovery of oil, and expressed it as his opinion and the opinion of many mid-continent engineers with whom he had discussed the matter, that if the liquid propane and butane thus introduced into the Burbank field had been gas-saturated, a great deal more would have been accomplished in the way of increased oil recovery.

In reply to query by Counsel, Witness explained his statement that the cooling process of the Wright patent was not practically operable as follows: That the average oil well would not have a diameter of over 10 or 12 inches and the inside casing in the majority of wells is 6 inch casing; that the Wright patent would require another string of casing, say 2″ pipe, to put the gas into the well, and that this gas entering the well would be warm, coming from the compression pipes; that Wright's proposal is to pump brine into the top of the casing around the gas inlet pipe and re*p*ly on thermal action for circulating the brine; that this would not be practically operative; that if you bring the brine into the casing on one side (indicating on enlarged chart reproduction of the Wright patent drawing) the brine will go across the casing and out through the outlet without circulation.

Replying to the Court's expressed opinion that Wright meant that the casing could be divided in half except at the bottom, Witness stated that that would be an extremely difficult proposition in an oil well because the casings of oil wells are circular pipes extending down into the well 34 1000 ft. or more; that (referring to the chart illustration of the Wright patent) there would have to be both inside and outside pipes extending down into the well; that the well casings have joints, ranging from 20 to 30 ft. in length, and it would be almost impossible to run a partition between the inside and the outside pipes because the pipes are not made to very close standards.

Replying to query by counsel, witness stated that Wright explained the method of getting circulation of brine in his patent as being entirely by thermal action.

Asked by the Court to specify whether by "thermal action" he meant that the cold would fall and the hot rise, Witness stated "Yes"; that the brine would be heated right at the top of the well in the Wright patent.

Queried by Counsel as to whether Wright can get circulation by thermal differential as he expects, witness stated that he failed to see how it would be possible.

Asked by Counsel to explain the practical difference between Doherty's idea for introducing liquid propane and butane saturated with gas into the well, and any previous use of natural gas containing as ingredients propane and butane—witness answered that whereas natural gas under pressure is a potential source of energy, such energy cannot be imparted to the oil unless the gas can be actually dissolved in the oil; that the pushing effect of the gas under pressure can only be used if the volume of oil is such as to prevent channeling of the gas through the sand. Continuing his answer, Witness cited experiments showing that a 10 ft. column of oil exposed to gas would take about 35 years to saturate the oil with gas unless there was agitation; whereas Mr. Doherty's process contemplates a
35 preliminary solution of the gas in the liquid propane and butane so that the gas is already in liquid solution when it enters the oil, so that the solution has this energy in it when it dissolves in the oil.

Queried by the Court as to whether the gaseous propane and butane is a liquid at the bottom of the well, Witness stated that the gas-saturated propane and butane is a liquid and that as this liquid goes into the sand it dissolves in the oil and that in going out of solution in the oil as a gas it pushes the oil toward the outlet well or the point of reduced pressure. Illustrating this to the Court by means of the samples of sand in evidence (Exhibit "C") Witness explained that gas can be forced through the sand without driving oil out of the sand, but that if liquid propane and butane were put into the sand sample lots of oil could be recovered from the sample, gas serving as a driving medium to put the liquid through the sample.

Witness stated, in reply to query by Counsel, that the gas-saturated liquid propane and butane which Doherty proposes to use on the oil makes the oil thin, reduces its viscosity, reduces its surface tension so that it will not adhere to the sand grains, increases its volume and decreases its gravity.

Answering the Court's query as to wherein the Doherty patent differs other than in degree from the Wright patent,

and the Court's statement that the Wright patent "has propane and butane in it, and it has natural gas, and it has been liquefied to some extent", witness stated that in addition to the degree, Doherty's process contemplates carrying large quantities of energy, and that it is the combination of the two that Doherty is after. Queried by the
36 Court as to whether there was subject matter of
invention in one person building a motor with 7 h. p. and another building one along the same lines with 14 h. p., witness answered that he did not know that one could say that there was invention in that case. Witness pointed out that he did not think the Wright patent contemplated any of the features that Doherty does in his, other than that he anticipated some recovery from gas drive, and he knew that gasoline, if the gas was properly cooled, would drop out as a liquid. In reply to query by the Court, Witness stated that the preliminary use of gas in the Wright patent was as a source of pressure, and that the object of brine cooling was the patentee's expectation that some gasoline would drop out and wash the sand to some extent.

Replying to queries by counsel, witness stated that he had examined the original file history of the Wright patent application; that he gained the idea from reading the Wright patent file that the patentee's original conception of his invention was that it involved broadly the putting of gas into the oil sand and the storing of gas in the sand, and that the patentee appeared hazy as to the amount of gasoline which could be condensed, seeming by his manner of referring to it to anticipate that almost the major portion of the gas would liquefy to gasoline.

Answering queries of the Court as to the chemical composition of propane, the witness stated that methane is the lightest member of the gaseous paraffine hydrocarbons and has a formula of CH_4; that ethane, the next heaviest member of the series, has a formula C_2H_6, and propane, the third member of the series, has a formula C_3H_8. The Court explained that the object of his query was to make sure
37 that no claim was made of "any anatomic changes"
in the application of the Doherty process, to which the Witness answered that he believed there were no such changes.

Counsel then read to the Witness claim 1 of the Doherty application as a condensed definition of the Doherty inven-

tion, and asked the witness to explain wherein the invention of the Doherty application represents an improvement in the art over what is shown by the Wright patent. Replying to this question, the witness referred to his prior testimony for such explanation and stated that it was chiefly a matter of delivering concentrated energy and a selective solvent to the sand for the purpose of obtaining the benefit near the producing well of the energy available in the form of propane and butane to deliver oil to the well, the Doherty process also making use of a byproduct which in the past has been wasted. Witness further explained that experiments indicated that the propane and butane are better recovery and energy-supplying agents when they carry gas in solution. Continuing the Witness stated that operations similar in principle to Wright's patent process have been going on for years, that gas carrying gasoline in the liquid state has been introduced into oil wells for years without any appreciable benefit over the method of simply putting in gas from which the gasoline has been extracted. Witness explained that the average gasoline content of every 1000 cu. ft. of natural gas is not over three-quarters of a gallon. Witness stated that in a recent check of operations his Company had treated an average of about 200,000,000 ft. of gas a day, at various points in the Midcontinent, and that the average gasoline content was about three-quarters
of a gallon per 1000 cu. ft. of gas. Witness repeated
38 that his Company had used Wright's general method
for a long time and after much study were convinced
that they had to improve on it.

Queried by the Court as to how near the compressor or field apparatus is to the extracting well, Witness stated that the gas distributing lines might all lead from a central plant and distribute over a wide area, or on the other hand, they may supply only one or two wells, in which latter case the plant would be within a few hundred or a thousand feet of the well. Witness stated that in one Kansas field he had some 800 wells and 81 injection wells in which there were about 25 to 30 miles of pipe in use for delivering from a central plant. In another field there were only two pressure injecting wells using only a matter of about 600 ft. of pipe.

Queried by Counsel as to the action of gas saturated propane and butane after it enters the well, witness (indicating on the chart illustrating the application of the Doherty invention) stated that it was difficult for him to express exactly what took place in the sand, but that he knew that as soon as the liquid was introduced the pressure in the structure immediately built up showing a dissolving action around the inlet well and that shortly after there are greater recoveries from the outlet well.

Replying to query by the Court, witness stated that the ideal time to use the Doherty process would be when the wells were first opened to production, but that practically, processes of this type w-re not put in use until after the field had been partially depleted.

Replying to query by Counsel concerning Witness's knowledge of any Patent Office decision on the question of invention which would appear to be in conflict with their adverse decision on this Doherty invention, witness testified that in granting the patent to Little 1,762,785, the Patent Office had recognized the presence of invention in the use of liquid propane and butane, as compared to the prior art disclosure and use of gasoline and naphtha, for dissolving rosins and terpenes from the cellular structure of wood. Witness went on to explain that the cellular structure of wood is closely analagous to the cellular structure of oil sand, that prior to the filing date of the application for the Little patent, gasoline, naphthas and various other liquid hydrocarbons had been used in the same way and for the same purpose as the liquid propane and butane described in the Little patent, and that Little's idea of employing liquid butane for extracting rosins from wood is analogous to the Doherty idea of removing oil from the pores of sand with propane and butane. 39

Replying to query by the Court, Witness stated that the process of the Wright patent is substantially in use except for the Wright method of well cooling. Witness explained that the method of the Doherty application was not in use because of lack of opportunity to apply the process near one of the gasoline plants where propane and butane was available, and because application of the Doherty process requires ownership or control of a big acreage in order to justify the expense of treatment without danger of losing oil to neighboring leases controlled by others. Witness stated that the Doherty process would undoubtedly be in use if his Company had a lease of sufficient size to be properly worked, and a gasoline plant conveniently located for supplying propane and butane.

Counsel then offered in evidence a complete file
40 history of the Little patent, including copies of the
principal file references cited by the Patent Office, as Plaintiff's Exhibit "N".

Replying to query by Counsel, Witness stated that the Wright patent process had been used substantially for many years and in some areas had proven quite successful in increasing production. Witness stated that in other areas the process had been tried and they had not been able to increase production appreciably. Witness anticipated that use of the Doherty process would increase production four or five times what they would anticipate by normal operation over a period of ten or twelve years. Citing an example, witness stated that if over a period of ten years we anticipated an average recovery of 100 barrels per day from a certain property, the process of the Doherty application if put into effect should, he thought, over a period of ten or twelve years yield probably 400 or 500 barrels per day, as indicated by results accomplished; that in using the method outlined in the Wright patent they considered themselves fortunate if they could double the production anticipated over a few years; that on the average, they do not even double their production by employing the Wright patent process or what they call "the gas drive".

Queried by Counsel as to whether there was any mention of Mr. Doherty's gas-saturated propane-butane medium in the Wright patent, Witness answered "No," and continued that the only thing mentioned by Wright is that gasoline will condense in his method. Witness stated that the work done by Mr. Doherty was the first that they had
been able to find any record of, after a search of the
41 literature, giving knowledge of the effect of dis-
solved gas on the viscosity of oil. In reply to a further query, Witness stated that he did not think that Wright had any knowledge of the superiority over gasoline for his purpose of a gas-saturated propane-butane material such as that described by Doherty.

In closing the direct examination, Counsel for Plaintiff apologized for any apparently illogical order in which the testimony was presented, explaining this defect by the effort to present the case in the brief period allotted by the Court for the hearing.

Plaintiff rests.

Counsel for Defendant presented no witnesses but offered in evidence the following exhibits:

(1) A printed copy of the Wright patent No. 1,101,605.

(2) Pages 438 to 440, inclusive, of the American Petroleum Industry, Bacon and Hamor, Vol. 2, 1916.

(3) The Patent Examiner's Statement.

(4) The decision of the Patent Office Board of Appeals.

The foregoing exhibits were received and marked "Defendant's Exhibits 1, 2, 3 and 4, respectively".

Cross-examination:

Replying to query by Counsel for Defendant, addressed to the Witness, Counsel for plaintiff (interposing) explained that the Doherty application in suit has no drawing, and that the chart presented at the hearing was simply to illustrate the practical application of the Doherty invention.

Answering further queries of Counsel for Defendant, the Witness stated that he believed that the Doherty application contained no explanation of the manner in which the liquid propane and butane was cooled, the application simply explaining that propane and butane was liquefied and saturated with natural gas. 42

Replying to queries of counsel for Defendant as to whether it was not a fact that natural gas or liquid as it flows into the pressure well is merely natural gas that is enriched with propane and butane, the witness explained that it was propane and butane enriched with natural gas, and that the mixture would probably not include the heavier components of natural gas which make up gasoline, but would include propane and butane saturated with ethane and methane. Witness explained that the hexanes and heavier hydrocarbons would not be included because they would have been extracted. Witness agreed that the first four gases of the paraffine series, methane, ethane, propane and butane, are gaseous at normal temperature and pressure, and that they can be liquefied by increased pressure and at lowered temperatures. Witness stated that depending upon the vapor pressures of the mixture of these four gases they would all liquefy to some extent, and that in general they are all found in natural gas. Witness further stated that methane is the chief ingredient of natural gas, and that in the Doherty process the liquid propane and butane is saturated with methane; that the liquid propane and butane will dissolve many times their volume of methane and ethane, and that these gases go together with the propane and butane into the oil sand. Witness further stated that when the pressure is reduced a certain percentage of methane will go out of solution, thus becoming available in the form of energy.

43 Asked about what temperature and pressure is used to reduce these normally gaseous hydrocarbons to liquid, witness stated that these varied with gasoline plant operation, explaining that the compressor plants usually operate at around 250 to 300 lbs. pressure for making gasoline, and that the propane and butane can be taken off at these pressures as a liquid by means of fractionating equipment.

Queried as to the temperature, Witness stated that he could not answer exactly as to the temperatures employed in the rectifying towers but stated that these temperatures would vary with the pressure. Witness stated that he could produce a curve which would show at what temperatures and pressures these gases are liquid. Queried further on this point, Witness stated that propane can be liquefied at a temperature of 90° F. when under a pressure of approximately 150 pounds gauge, and that pure butane will liquefy at 90° F. under a pressure of approximately 30 pounds. Replying to further queries, Witness stated that there was no way, at the start, of telling from which wells oil would be produced when one of a group was used as a pressure well for introducing the liquid propane and butane, unless very good results had been obtained from coring the sand. Explaining, Witness stated that sometimes the well cores would indicate the wells in which the sands were of more or less analogous great porosity, and that after starting to put the pressure medium into the well the offset wells which first showed increased gas production would be the ones from which increased oil production would be anticipated.

Queried as to whether the Wright patent filed in 1912 could be regarded as originating the broad idea of having one pressure well to force oil out of the other wells,
44 Witness stated that he believed not; but believed that this process was carried on several years prior to Wright in Ohio. Witness verified as correct Counsel for Defendant's explanation that the purpose of the last question was to show that neither Wright nor Doherty was entitled to the broad idea of using one well for a pressure well in forcing oil out of the others. Counsel for defendant suggested that an illustration of oil viscosity would be that of dropping gasoline into the crank case of an automobile, thus reducing the viscosity of the oil in the crank case. Witness agreed. Counsel then asked whether the principle of this testimony was not that a light oil such as gasoline mixed with a heavy oil will reduce the viscosity of the latter and also loosen the surface tension. Witness answered in the affirmative and pointed out that in addition the gas dissolved under pressure will do the same thing in the oil.

This concluded the cross-examination.

Redirect examination:

Explaining that counsel for defendant had apparently been trying to draw an analogy between the action of the gas saturated propane and butane of Doherty and a reduction of viscosity of oil in a crank case by addition of gasoline, Counsel for Plaintiff asked Witness if the gas-saturated propane and butane of the Doherty application performed any other function than that of reducing the viscosity of the oil. Witness pointed out that the gas-saturated liquid propane and butane of the Doherty invention had a solvent action on the oil films attached to the sand grains closely analogous to the solvent action exerted by the liquid propane and butane for removing rosin and terpenes from the cellular wood structure in accordance with the process of the Little patent Exhibit "N".
45 Witness explained that these fine films of oil adhering to the sand grains cannot be removed without a solvent, and constitute a very large percentage of the total volume of oil in the sand; that estimates of many compe-

tent engineers checked by field calculations and field experiments show that the present methods only recover from 15 to 30 per cent of the oil originally in the sand, and that actual mining tests in Alsace Lorraine found that only 16-2/3 per cent of the oil was actually recovered by the wells and the balance could only be recovered by bringing the sand to the surface and treating it. Queried by Counsel as to whether gas-saturated propane and butane employed in accordance with the Doherty process would recover a considerable amount of this excess oil left in the sand unrecoverable by application of present known methods, Witness stated that it should.

Defendant rests.

Whereupon, at 3:30 o'clock P. M. the trial of the foregoing case was concluded.

Be it further remembered that the foregoing contains the substance of all of the evidence given on the hearing of this cause, and each of the exceptions stated to have been taken by the attorney for the plaintiff were so taken and were duly allowed and noted by the Court, and in order that each and every one thereof may be preserved and made of record this Statement of Evidence is duly stated, approved and signed, and ordered to be made of record in the above entitled cause this 14th day of June, 1932.

By the court:

DANIEL W. O'DONOGHUE,
Justice.

46 In the Supreme Court of the District of Columbia.

In Equity.

51214.

Henry L. Doherty, Plaintiff,

vs.

Thomas E. Robertson, Commissioner of Patents,
Defendant.

Stipulation.

It is agreed between the parties hereto that the papers offered in evidence as exhibits for the plaintiff and defendant shall form a part of the Statement of Evidence and the portions thereof referred to in the Designation of Record may be printed as a part of the record on appeal to follow the statement of evidence.

J. AUSTIN STONE,
Of Counsel for Plaintiff.
T. A. HOSTETLER,
Of Counsel for Defendant.

Washington, D. C., July 26, 1932.

47 PTF'S EX. A'.

390.

Department of Commerce, United States Patent Office.

To all persons to whom these presents shall come, Greeting:

This is to certify that the annexed is a true copy from the records of this office of the Petition, Specification and Oath, as it now stands, in the matter of the Pending Application of Henry L. Doherty, filed February 12, 1927, Serial Number 167,865, for Improvement in Method of Recovering Oil from Oil Sands.

In testimony whereof I have hereunto set my hand and caused the seal of the Patent Office to be affixed, at the City of Washington, this eleventh day of January, in the year of our Lord one thousand nine hundred and thirty-two and of the Independence of the United States of America the one hundred and fifty-sixth.

[Seal Patent Office, United States of America.]

THOMAS E. ROBERTSON,
Commissioner of Patents.

Attest:
D. E. WILSON,
Chief of Division.

48 Mail Room, U. S. Patent Office, Feb. 12, 1927.

167,865.

Petition.

To the Commissioner of Patents:

Your petitioner, Henry L. Doherty, a citizen of the United States of America, residing at New York, in the County of

New York, State of New York, whose Post Office address is 60 Wall Street, New York, N. Y., prays that Letters Patent may be granted to him for improvements in method of recovering oil from oil sands as set forth in the annexed specification, and he hereby appoints Edmund G. Borden, 60 Wall Street, New York City, Registration No. 3870, his attorney, with full power of substitution and revocation, to prosecute this application, to make alterations and amendments therein, to sign the drawings, to receive the Patent, and to transact all business in the Patent Office connected therewith.

HENRY L. DOHERTY.

49 *Specification.*

To all whom it may concern:

Be it known that I, Henry L. Doherty, a citizen of the United States of America, residing at New York, in the county of New York, State of New York, have invented certain new and useful improvements in method of recovering oil from oil sands, and I do hereby declare the following to be a full, clear and exact description of the invention, such as will enable others skilled in the art to which it appertains, to make and use the same.

This invention relates to the recovery of oil from oil sands and more particularly to a method of recovery of oil from a depleted or partially depleted oil sand body.

It is a well known fact that only a relatively small proportion of the oil naturally occurring in an oil sand is recovered by present methods of oil production. My invention has for its object to provide a process that may advantageously be used for more completely draining a previously treated oil sand of its oil.

At the present time a large amount of gasoline is obtained by the treatment of natural gas to recover the gasoline
which is absorbed or entrained by the gas. In treat-
50 ing natural gas to recover its gasoline content a by-
product is obtained which is composed principally of propane and butane. The propane and butane mixture is usually collected under pressure so that it remains in liquid form and if the process of recovering the propane and butane from casing head gasoline is carried on under sufficient pressure, liquid ethane may also be recovered. Further-

more, it is difficult to separate the propane and butane from gasoline without including some pentane.

The present invention relates more particularly to the use of the by-product mixture composed principally of propane and butane, although it is to be understood that this liquid mixture may contain ethane and pentane.

According to my invention I utilize said liquid by-product for assisting in the recovery of oil from the oil sands. A liquid butane-propane mixture will dissolve extremely large quantities of natural gas, the amount dissolved depending on the chemical constitution of the gas. If the gas contains a high percentage of ethane it has been found that one volume of said liquid mixture will absorb more than 200 volumes of such gas. The resultant liquid mixture is of extremely low viscosity and of very low surface tension. The resultant mixture is furthermore readily soluble in petroleum oil and when dissolved in the oil the resultant oil has a very much lower viscosity and surface tension than it originally had.

In carrying out my invention I maintain said liquid by-product under high pressure and saturate it with a hydrocarbon gas. The resultant mixture is then pumped into the sands in which the oil is located and on account of its
51 low viscosity and low surface tension readily penetrates through the sands. In passing through the sands the mixture dissolves in the oil with the result that the viscosity and surface tension of the oil are lowered. Preferably a pressure is maintained in the sands by closing the well outlets and the liquid by-product is inserted under considerable pressure to force the liquid to penetrate through the sands. When the pressure is removed the gas dissolved in the liquid by-product and in the oil tends to come out of the solution and to expand in the same way that the original gas dissolved in the oil expands. This expansion or foaming of the oil in the sands causes a movement of the oil through the sands toward the opening. None of the gas originally dissolved in the by-product liquid will remain dissolved in the liquid at the temperatures existing in the earth, when the pressure is lowered to substantially atmospheric pressure. Therefore substantially all of the gas will be released and its expansive force rendered effective for moving the oil through the sand.

I have discovered that it is comparatively difficult to dissolve gas in the oil while the oil is held in the pores of the sand. In accordance with the present invention it is possible to effect a greater solution of the gas in the oil, due to the fact that the gas is carried through the sands by the liquid by-product in a liquid form. The diffusion of the liquid by-product into the oil is very much more rapid than the diffusion of the gas into the oil. Accordingly, the liquid by-product forms a convenient means by which the gas may be dissolved in the oil. At the same time the liquid by-product is also dissolved in the oil and both products therefore tend to greatly lower the surface tension and the
52 viscosity of the oil.

The method of the present invention is applicable more particularly to the recovery of oil from sands in a depleted or partially depleted field. In view of the fact that the liquid hydrocarbon mixture and the natural gas used in the present process are valuable constituents it is desirable that the present method be applied to the operation of the field as a unit because when the liquid mixture and the gas are forced into the sands under pressure it is impossible to confine the migration of these products through the sands. It is practicable however to utilize the present method in a portion of the field provided this portion is sufficiently large to include the area which might be effected by the introduction of the liquid mixture and gas. In any event however it is necessary to be able to close the wells and to control the pressure in the sands. It will be obvious therefore that a unit development of a pool or field will be very much more satisfactory in controlling the pressure and the migration of the gas and liquid mixture through the sands.

What I claim is:

1. A method of obtaining oil from oil fields comprising forcing a liquefied mixture of butane and propane saturated with hydrocarbon gas into an oil stratum, and recovering oil from the stratum at a point remote from the point of introduction of the mixture into the stratum.

2. A method of obtaining oil from oil fields comprising forcing a liquefied mixture of butane and propane saturated with hydrocarbon gas under high pressure into an

oil stratum under a relatively lower pressure, and
53 recovering oil from the stratum at a point removed
from the point of introduction of the mixture into
the stratum.

3. A method of obtaining oil from oil fields comprising forcing a liquefied mixture of butane and propane saturated with hydrocarbon gas under high pressure into an oil stratum, and recovering oil from the stratum at a point of relatively low pressure.

4. A method of obtaining oil from oil fields comprising forcing a liquefied hydrocarbon substance consisting of butane and propane with gas in solution under high pressure into an oil stratum and withdrawing oil from the stratum at a point of relatively low pressure.

5. A method of obtaining oil from oil fields comprising forcing a mixture of hydrocarbon constituents having a molecular structure including less than six carbon atoms into an oil stratum and recovering oil from the stratum.

6. A method of obtaining oil from oil fields comprising forcing a liquefied mixture of hydrocarbon constituents having a molecular structure including less than six carbon atoms into an oil stratum and recovering oil from the stratum.

7. A method of obtaining oil from oil fields comprising forcing a gas-saturated liquefied mixture of hydrocarbon constituents having a molecular structure including less than six carbon atoms into an oil stratum and recovering oil from the stratum.

8. A method of obtaining oil from oil sands comprising introducing into the stratum in the earth containing oil a liquid hydrocarbon mixture having a gravity, viscosity and surface tension lower than gasoline and withdrawing oil
and the liquid mixture from a portion of the stratum
54 different from that in which the liquid mixture is
introduced.

9. A method of obtaining oil from oil fields comprising introducing under pressure into the stratum containing the oil a hydrocarbon liquid which contains more than 100 volumes of gas in solution per volume of liquid, driving the liquid mixture, gas and oil through the sands to an outlet and withdrawing the mixture of oil, gas and liquid

mixture through a well different from that in which the liquid mixture and gas are inserted into that stratum.

10. A method of obtaining oil from oil fields comprising forcing under pressure a mixture of hydrocarbon constitutents having a molecular structure each less than six carbon atoms and containing many times its volume of gas in solution into one portion of a sand stratum containing oil and recovering oil, hydrocarbon liquid and gas from the oil stratum at a point removed from the point of introduction of the mixture and gas into the stratum, said point being of relatively lower pressure than the point of introduction of the mixture into that stratum.

11. The process of recovering oil from oil-bearing strata consisting in subjecting the oil-bearing strata to the action of a hydrocarbon gas saturated liquid propane-butane mixture introduced under pressure into the strata whereby the oil in the strata is subjected to the motivating action of both liquid and gas.

In testimony whereof I affix my signature.

HENRY L. DOHERTY.

55 *Oath.*

COUNTY OF NEW YORK,
State of New York, ss:

I, Henry L. Doherty, the above-named petitioner, being duly sworn, depose and say that I am a citizen of the United States of America and resident of New York, N. Y. and that I verily believe myself to be the original, first and sole inventor of the improvements in method of recovering oil from oil sands described and claimed in the annexed specification; that I do not know and do not believe that the same was ever known or used before my invention or discovery thereof, or patented or described in any printed publication in any country before my invention or discovery thereof, or more than two years prior to this application, or in public use or on sale in the United States for more than two years prior to this application; that said invention has not been patented in any country foreign to the United States on an application filed by me or my legal representatives or assigns more than twelve months prior to this application; and that no application for patent on said improvements has been filed by me or my representatives or assigns in any country foreign to the United States.

HENRY L. DOHERTY.

Subscribed and sworn to before me this 9th day of February, 1927.

[SEAL.] JAMES J. DELANEY,
Notary Public.

Bronx County Clerk's No. 85.
Certificate filed in New York Co. No. 498.
Commission expires March 30, 1928.

56 Compared by C. P., L. S. Revised by L. A. M. Letter No. 186,689. Date: Jan. 6/32.

57 Patent Office, Mailed May 29, 1928.

JK:MLA.

United States Patent Office.

Before the Board of Appeals, on Appeal.

In re Application of Henry L. Doherty. Ser. No. 167,865. Filed Feb. 12, 1927. For Method of Recovering Oil from Oil Sands.

Examiner's Statement.

An appeal has been taken from the final rejection of the following claims:

1. A method of obtaining oil from oil fields comprising forcing a liquefied mixture of butane and propane saturated with hydrocarbon gas into an oil stratum, and recovering oil from the stratum at a point remote from the point of introduction of the mixture into the stratum.
2. A method of obtaining oil from oil fields comprising forcing a liquefied mixture of butane and propane saturated with hydrocarbon gas under high pressure into an oil stratum under a relatively lower pressure, and recovering oil from the stratum at a point removed from the point of introduction of the mixture into the stratum.
3. A method of obtaining oil from oil fields comprising forcing a liquefied mixture of butane and propane saturated

with hydrocarbon gas under high pressure into an oil stratum, and recovering oil from the stratum at a point of relatively low pressure.

4. A method of obtaining oil from oil fields comprising forcing a liquefied hydrocarbon substance consisting of butane and propane with gas in solution under high pressure into an oil stratum and withdrawing oil from the stratum at a point of relatively low pressure.

5. A method of obtaining oil from oil fields comprising forcing a mixture of hydrocarbon constituents having a molecular structure including less than six carbon atoms into an oil stratum and recovering oil from the stratum.

6. A method of obtaining oil from oil fields comprising forcing a liquefied mixture of hydrocarbon constituents having a molecular structure including less than six carbon atoms into an oil stratum and recovering oil from the stratum.

58 7. A method of obtaining oil from oil fields comprising forcing a gas-saturated liquefied mixture of hydrocarbon constituents having a molecular structure including less than six carbon atoms into an oil stratum and recovering oil from the stratum.

8. A method of obtaining oil from oil sands comprising introducing into the stratum in the earth containing oil a liquid hydrocarbon mixture having a gravity, viscosity and surface tension lower than gasoline and withdrawing oil and the liquid mixture from a portion of the stratum different from that in which the liquid mixture is introduced.

9. A method of obtaining oil from oil fields comprising introducing under pressure into the stratum containing the oil a hydrocarbon liquid which contains more than 100 volumes of gas in solution per volume of liquid, driving the liquid mixture, gas and oil through the sands to an outlet and withdrawing the mixture of oil, gas and liquid mixture through a well different from that in which the liquid mixture and gas are inserted into that stratum.

10. A method of obtaining oil from oil fields comprising forcing under pressure a mixture of hydrocarbon constituents having a molecular structure each less than six carbon atoms and containing many times its volume of gas in solution into one portion of a sand stratum containing oil and recovering oil, hydrocarbon liquid and gas from the oil stratum at a point removed from the point of introduc-

tion of the mixture and gas into the stratum, said point being of relatively lower pressure than the point of introduction of the mixture into that stratum.

11. The process of recovering oil from oil-bearing strata consisting in subjecting the oil-bearing strata to the action of a hydrocarbon gas saturated liquid propane-butane mixture introduced under pressure into the strata whereby the oil in the strata is subjected to the motivating action of both liquid and gas.

Reference relied upon is Wright, 1,101,605, June 30, 1914.

The invention relates to a process of recovery of oil from a depleted or partially depleted oil sand body and the process consists of forcing under pressure a liquified 59 hydrocarbon substance consisting principally of butane and propane which may also carry some ethane and pentane, saturated with a hydrocarbon gas, such as methane, into the oil stratum through a well and obtaining products carried by such substances as it passes through the oil bearing stratum and out therefrom at a point remote from the point of introduction, or through another well remote from the well through which the substance has been introduced.

The specification states that such a liquified mixture of Butane-Propane has a great capacity of dissolving the hydrocarbon gas and the whole dissolves in the heavier oil encountered in the stratum and by doing so it makes the heavier oil less viscous whereby it is capable of flowing more readily.

The hydrocarbons methane, ethane, propane, butane and penthane are the first five members of the homologous parafin series having respectively the formulæ:

$$CH_4,\ C_2H_6,\ C_3H_8,\ C_4H_{10},\ \text{and}\ C_5H_{12},$$

and these hydrocarbons at ordinary temperature and pressure remain in the gaseous states; the next member of the series hexane C_6H_{14} is a liquid under ordinary condition of temperature and pressure but is still very volatile and usually is removed from the modern stabilized gasoline.

It is thought the patent to Wright anticipates the process which is correctly defined by the claims such as claim 1 or any other claim of record. Wright stores oil and gas obtained from a well in his tank 3 and draws the uncondensed gases collected at the top of the tank into the com-

pressor 6, liquifies the contents and introduces it into a well
and collects the products from another well. At ordinary
temperature the only gases that will collect at the top of
the tank will be methane, ethane, propane, butane,
60 pentane and it is probable that some of the more
volatile liquids such as hexane will have some of it
in a gaseous state. Upon compression of such gaseous extract from the tank 3 methane will remain in the gaseous state since its critical temperature is —115° F. and no such cooling is contemplated by Wright as to reach the critical temperature of methane (Marsh Gas) since the cooling is accomplished by cold brien and —115° F. cannot be obtained by such means. All the remaining gases will be liquified and a mixture of liquified hydrocarbon substance comprising propane but butane and some ethane, penthane as also small quantities of the more volatile parafins saturated with the gaseous hydrocarbon (Methane) will be introduced under pressure into the oil stratum performing all the functions inherent thereto and the products obtained will be extracted from another well, thus substantially performing the process defined by the claims. Applicant's argument that there may be no methane (Marsh gas) present is not believed to be correct since the table on page 439 of Bacon and Hamor, American Petroleum Industry (copy in Div. 38) indicates that in the natural gas obtained from various fields Marsh gas or methane is the chief constituent running from 53 to 99% in various fields and no example is given wherein no marsh gas was present.

It appears, therefore, that Wright anticipates applicant's process even though Wright does not state that the liquified hydrocarbons will be saturated with a gaseous hydrocarbon nor does he state what hydrocarbons will be present. The term gazoline is rather a loose term and its consistency is not permanent. However, from the
nature of the steps performed by Wright as de-
61 scribed in the patent it appears he carries out sub-
stantially the process of the application and the
mere fact that some of the higher hydrocarbons (above 5 carbon atoms) may be carried along does not appear to patentably distinguish the process since it is not seen that their presence will affect the process in any way.

The original specification contained ten claims and claim 11 has been introduced with the statement of the appeal; the claim is anticipated in the same manner as the remaining claims and no objection is interposed by the Examiner to claim 11 being made of record.

Respectfully submitted,

C. F. KRAFFT,
Examiner, Div. 38.

May 29, 1928.

62 Appeal No. 2347, Paper No. 9.

Decision.

MCV.

U. S. Patent Office, Board of Appeals, Oct. 3, 1929, Mailed.

Appeal No. 2347.
Hearing: March 20, 1929.

In the United States Patent Office.

Before the Board of Appeals.

Ex Parte HENRY L. DOHERTY.

Application for Patent. Filed Feb. 12, 1927. Ser. No. 167,865. Method of Recovering Oil from Oil Sands.

Mr. Edmund G. Borden for applicant.

This is an appeal from the final rejection by the primary examiner of claims 1 to 11, inclusive.

Claim 1 is illustrative and reads as follows:

1. A method of obtaining oil from oil fields comprising forcing a liquefied mixture of butane and propane saturated with hydrocarbon gas into an oil stratum, and recovering oil from the stratum at a point remote from the point of introduction of the mixture into the stratum.

The reference relied upon is Wright, 1,101,605, June 30, 1914.

The alleged invention relates to a method of recovering oil from a partially depleted oil sand body. Appellant forces under pressure a liquefied hydrocarbon substance through a well into the oil stratum where it dissolves in the oil, lowering the viscosity and surface tension of the latter. The product passes out through another well.

The claims stand rejected on the patent of Wright. The first claim of said patent to Wright, reading as follows:

> 1. A method of obtaining oil from exhausted wells which consists in forcing a liquefied natural gas substance into an oil bearing stratum at one point and receiving oil mingled with said substance at another point,

shows that Wright had a similar purpose in mind and
63 employed a similar process unless it be that he uses
a materially different liquid hydrocarbon mixture.

According to appellant's specification he uses a by-product obtained in treating natural gas to recover its gasoline, consisting principally of propane and butane collected under pressure so that it remains in liquid form and which may also contain some liquid ethane and pentane. This liquid by-product mixture is saturated with hydrocarbon gas before it is pumped into the oil sand.

Wright does not give the chemical composition of his mixture but states in his specification and claims that he uses liquefied natural gas, which may be the waste gas flowing from oil wells, or gas which evaporates from the oil in his gas-tight reservoirs.

In his statement the examiner says that methane (CH_4), ethane (C_2H_6), propane (C_3H_8), butane (C_4H_{10}), and penthane (C_5H_{12}) are gaseous hydrocarbons at ordinary temperature and that the next member of the series, hexane (C_6H_{14}), although liquid at ordinary temperature, is so volatile and unstable that it also is usually removed from modern stabilized gasoline. The examiner holds that the natural gas used by Wright must consist substantially of the above hydrocarbons, which also constitute appellant's mixture, and that these gases will be liquefied by Wright's process except the methane with which the liquid will be charged.

Appellant contends that the examiner's holding is based on erroneous assumptions, that Wright does not state what hydrocarbons are in his mixture, that higher hydrocarbons than hexane may be present and would be if Wright used the gas that evaporates from oil obtained from partially depleted wells, that the pressure and cooling agent used by Wright may not be such as to liquefy the propane and
butane and that Wright does not state that methane
64 gas is present in his mixture although appellant's
brief (page 9) admits that such gas would probably
be present "if Wright uses natural gas from some other source, as he may do."

It is thought unnecessary to discuss each of the eleven appealed claims. Some claims specify liquefied mixture of butane and propane, other claims, hydrocarbon having less than six carbon atoms to the molecule, and another claim, hydrocarbon "having a gravity, viscosity and surface tension lower than gasoline." Most, but not all, of the claims specify that the liquefied mixture contain- a hydrocarbon gas.

The examiner states his conclusion as follows:

> It appears, therefore, that Wright anticipates applicant's process even though Wright does not state that the liquefied hydrocarbons will be saturated with a gaseous hydrocarbon nor does he state what hydrocarbons will be present. The term gasoline is rather a loose term and its consistency is not permanent. However, from the nature of the steps performed by Wright as described in the patent it appears he carries out substantially the process of the application and the mere fact that some of the higher hydrocarbons (above 5 carbon atoms) may be carried along does not appear to patentably distinguish the process since it is not seen that their presence will affect the process in any way.

The examiner is the office expert in this art. After a careful consideration of the case and of appellant's argument we believe that the conclusion of the examiner is warranted and that appellant's contention that Wright is not a pertinent reference is untenable.

The decision of the examiner is affirmed.

M. J. MOORE,
Assistant Commissioner,
W. S. RUCKMAN,
Examiner-in-Chief,
EUGENE LANDERS,
Examiner-in-Chief,
Board of Appeals.

Oct. 3, 1929.

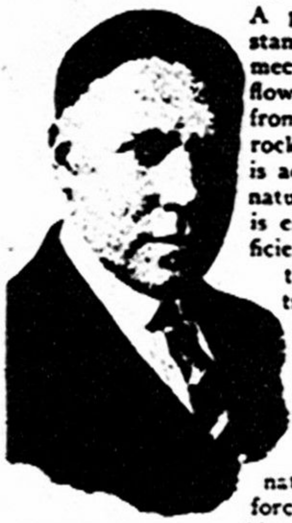
Endorsed on cover: District of Columbia Supreme Court. No. 5762. Henry L. Doherty, appellant, vs. Thomas E. Robertson, Commissioner of Patents. Court of Appeals, District of Columbia. Filed Aug. 9, 1932. Henry W. Hodges, Clerk.

Dissolved Natural Gas in Oil in Ground A Force That Aids Production

D-2

By Lester C. Uren
Professor of Petroleum Engineering, University of California, Berkeley

THE forces brought to bear by Nature in expelling petroleum from the pore spaces of the reservoir rock into wells drilled for oil recovery are of particular importance to the oil producer. A proper understanding of the mechanics of oil flow through and from the porous rocks in which it is accumulated by natural processes is essential to efficient well operation and control. The efficiency of recovery will depend to a large degree on the extent to which the natural expulsive forces are utilized. Improved methods of oil recovery must be based upon a full understanding of the mode of operation of the natural expulsive forces and be in harmony therewith.


LESTER C. UREN

In the first article of this series, printed in the January 19th issue of NATIONAL PETROLEUM NEWS, it was shown that, before an oil deposit is tapped by the discovery well, the oil and associated natural gas exist in a condition of pressure-temperature equilibrium; and that, due to the elevated pressure which usually prevails, a large volume of gas is forced into solution in the oil. By reason of this dissolved gas and the elevated temperature characteristic of deeply buried strata, the viscosity of petroleum is considerably reduced below that prevailing at normal atmospheric temperatures. Because of this reduced viscosity, it was suggested that the oils are in a condition to move with greater freedom through the porous reservoir rocks.

WHEN a reservoir sand containing oil charged with dissolved gas under high pressure is penetrated by a well, the equilibrium of forces that previously existed is disturbed. If the well is not shut in, and flow of fluids to the surface is permitted, the pressure within the reservoir sand in the immediate vicinity of the well is reduced. Reduction in pressure permits release of a part of the dissolved gas from the gas-saturated oil, and the gas thus released assumes the form of minute bubbles distributed through the viscous oil mass.

These bubbles, when first formed, are still under relatively high pressure, but as the pressure is further diminished, they expand. The effect is, literally, a physical expansion of the oil to a new volume many times its original size, an expansion which causes a part of the oil to be forced through the sands toward the centers of reduced pressure about the wells.

The potential expulsive effect of expanding gas originally dissolved in the oil may be demonstrated by recalling the data on gas solubility presented in the first article. It was shown, for example, that what was called the "approximate average" of eight different crudes was capable of dissolving about 105-cubic feet of natural gas per barrel at 500-pounds pressure.

THE solubility was found to be directly proportional to the pressure; hence, at 1000-pounds per square inch, a barrel of crude oil would be capable of retaining approximately 210-cubic feet of gas in solution, and at 1500-pounds, 315-cubic feet. Let us assume that a virgin oil pool has a "rock pressure" of 1000-pounds per square inch and that each barrel of oil contains 210-cubic feet of gas in solution. A barrel of oil occupies 5.6-cubic feet, and each cubic foot of oil would therefore contain 37.5 cubic feet of dissolved gas. Now, if the pressure is reduced to atmospheric, and the gas thus released from solution is retained within the oil in the form of bubbles, each cubic foot of the original oil will expand until it occupies 38.5-cubic feet (37.5 plus 1). The space within the oil sand available for the storage of oil and gas, however, remains constant, and, in order that expansion to atmospheric pressure may occur, 97% (37.5 divided by 38.5) of the oil and gas must be expelled from the sand into wells. The theoretical recovery of oil by gas expansion from 1000-pounds initial pressure, should therefore be 97%. From 500-pounds initial pressure, it would be nearly 95%.

WHILE the theoretical maximum recovery of oil from the reservoir sand by gas expansion is high, practically the expansive effect of the dissolved and occluded gas is very imperfectly applied, so that the actual efficiency of extraction is much lower. Actual recoveries[1] in producing fields are reported to be as low as 15 or 20% by many authorities.[2] Mining operations within the oil sands in the Pechelbronn oil field in Alsace have indicated that the total recovery by producing to the lower limit of economic recovery through wells, was only 16.7% of the total original oil content.[3] Recovery estimates for the Bradford field of Pennsylvania by ordinary methods of flowing and pumping, are placed by Mr. David White[4] of the U. S.

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[1] Lewis, J. O. "Rejuvenation of Depleted Fields," Record of Public Hearings before the Federal Oil Conservation Board, Washington, February, 1926.

[2] Lewis, J. O., "Methods of Increasing the Recovery of Oil from Wells," U. S. Bureau of Mines Bull. 148. See particularly pages 25-32.

[3] De Chambrier, P., "Working of Petroleum by Means of Shafts and Galleries," Journal, Inst. of Petroleum Technologists, London, Vol. 7, pages 178-189.

[4] White, D., Address before the Northwestern Pennsylvania Oil Producer's Assoc., October, 1924. See Oil City Derrick, April 20, 1925.

BASIS OF CONSERVATION ISSUE EXPLAINED BY UREN

THIS second article in the new series on improved production methods appearing exclusively in National Petroleum News is most timely, in that it gives the reader the fundamental facts that have been learned the past few years on the effect of natural gas on oil held in the ground.

These facts are the basis of the present thought and discussion within the industry on the desirability of legislation forcing producers to hold back-pressures on their wells. The knowledge that has been gained, through research work and experiments, of the natural aid gas exerts in forcing oil from the ground has made some people believe the holding of the gas in the ground to aid production should be compulsory.

This is only one development in improved production practice come to light in recent years that may greatly affect actual methods in use in oil fields. These developments generally are to be reviewed by Prof. Uren in this series of articles.

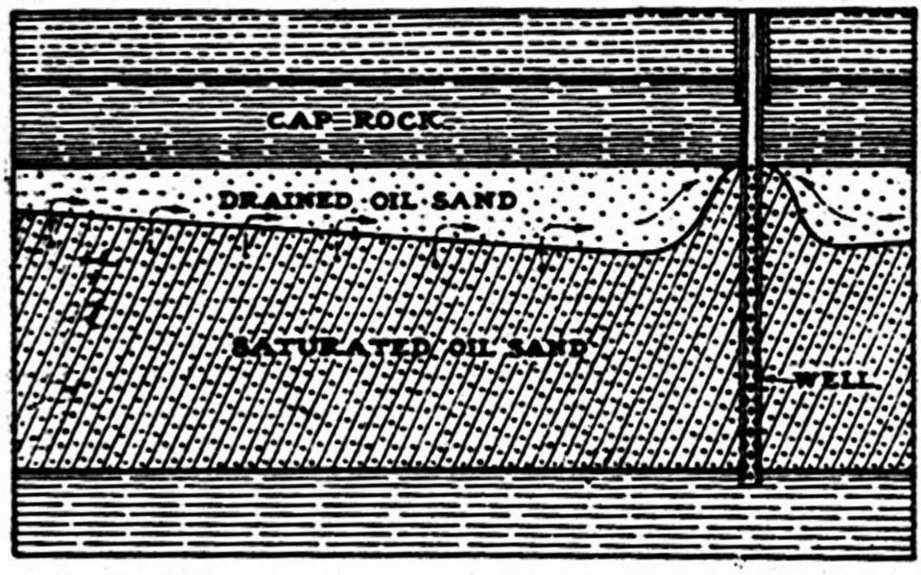

Fig. 1—Sketch illustrating escape of gas through partially drained channel in top of oil sand

Geological Survey, as low as 12½ per cent.

The reason for the low efficiency of gas expulsion in all probability lies in the fact the gas does not remain occluded within the oil after it is released from solution, but escapes to the well outlets by translation through the oil, or through oil-drained channels above or within the oil mass. (See Figure 1). Gas moves with greater freedom than oil through the minute spaces of the reservoir sand, and monopolizes the drainage channels to the exclusion of the more viscous and slow-moving oil.

THAT the efficiency of gas expulsion is low can be demonstrated by comparing the relative volumes of gas and oil produced from oil wells. In many fields during the period of "flush" production, wells produce from 1000 to 4000 cubic feet of gas per barrel of oil. If the rock pressure is 500-pounds per square inch, an average barrel of oil is capable of absorbing about 105-cubic feet of gas; but if 1000-cubic feet of gas flow from the well with each barrel of oil, it is clear that about nine times as much gas is being produced as the oil is capable of dissolving at the prevailing pressure.

In other words, if we assume that all the gas was originally dissolved in the oil, each barrel of oil brought to the surface is produced only at the expense of gas from nine barrels of "dead" oil left in the sand. In this case, the efficiency of gas expulsion, due to escape of the gas from the oil in the sand, is only 10%, and with higher gas-oil ratios, the efficiency will be correspondingly reduced. Gas-oil ratios can seldom be reduced below 500-cubic feet per barrel in a flowing well, and, unless large quantities of gas are supplied from sources outside the oil mass, it would therefore seem that the efficiency of gas expulsion may only occasionally exceed 20%.

If we assume that crude petroleum as stored within the earth is saturated with gas under high pressure, when the pressure is partially reduced by drainage of some of the oil and gas through wells, a portion of the dissolved gas will be released and will assume the form of minute bubbles. Each pore cell within the oil sand contains one or more gas bubbles, spherical in form in so far as the form of the pore spaces permit, and separated from each other by films of oil which occasionally break to permit two or more small bubbles to form larger ones.

In this stage, the oil and gas mixture may be regarded as of the nature of an emulsion, the gas being the internal phase. When first formed, these bubbles are exceedingly minute, but are still under high pressure; and as the pressure within the oil reservoir is gradually reduced, they continually expand, forcing the oil toward the well outlets. The pressure within the sand, of course, is not uniform, but increases progressively as the distance from the well increases. Each expanding bubble can therefore displace oil only in one direction: that is, toward the locus of reduced pressure within the well.

WE can perhaps, best explain the mechanics of gas expulsion by reference to Figure 2 illustrating a portion of a drainage channel composed of a series of communicating sand pores, terminating at the wall of a well. Only a few pore cells are shown constituting that portion of the drainage channel in the immediate vicinity of the well; but it will be understood that a multitude of communicating pore cells extend the channel indefinitely toward the right from the sketch. The wall of an intersecting well is assumed to be at the left of the sketch.

Originally, all cells were under uniform pressure, and all gas dissolved in the oil, but, when release of pressure within the well disturbs the equilibrium, one or more gas bubbles form in each cell. That formed in cell No. 1, nearest the well, promptly escapes to the well, carrying some of the surrounding and intervening oil with it. Release of pressure due to evacuation of the gas and a part of the oil from cell No. 1, creates a differential pressure between it and cell No. 2.

The gas bubble formed in cell No. 2 therefore expands and escapes to cell No. 1, where it undergoes further expansion and then escapes to the well, carrying with it a little of the oil from cell No. 2 and some of that left in cell No. 1 after the escape of its original gas bubble. In the same way, a bubble of gas passes from cell No. 3 to No. 2, thence to No. 1 and to the well, carrying along some of the oil which fills the intercommunicating capillary channels with each successive expansion.

IF the reader will now visualize a channel, perhaps hundreds of feet in length, composed of many thousand such pore cells, containing bubbles occasionally moving from pore to pore, accompanied by simultaneous displacement of oil, he will have grasped the modern conception of the mechanics of gas expulsion. The drainage system of a well consists of a multitude of such channels, radiating outward in all directions from the well, and communicating with each other, both laterally and vertically.

The influence of the reduced pressure within the well gradually extends outward in all directions from the well as a center, each pore cell traversed by the gas bubbles representing a definite pressure loss. When these increments of pressure loss build up to a total equivalent to the difference between the "rock pressure" and the pressure within the well, the system comes into equilibrium and no further movement of gas or oil toward the well occurs. This determines the normal radius of drainage of the well, and it is apparent that the drainage radius under such conditions will vary directly with the differential between the maximum rock pressure and the pressure maintained within the well.

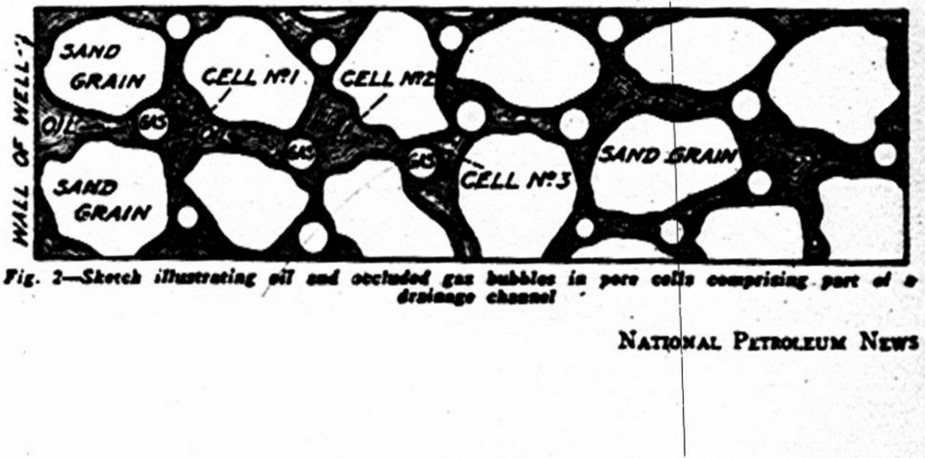

Fig. 2—Sketch illustrating oil and occluded gas bubbles in pore cells comprising part of a drainage channel

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[3] For a good explanation of oil expulsion by occluded gas expansion, the reader is referred to that by Mr. S. J. Dickey, in "American Petroleum—Supply and Demand," pages 32-36. This is the report of the Committee of Eleven, American Petroleum Institute, to the Federal Oil Conservation Board, published in book form by the McGraw-Hill Book Co., in August, 1925.

Measuring Natural Forces That Hold Back Flow of Oil in Ground

By Lester C. Uren
Professor of Petroleum Engineering, University of California, Berkeley

TWO natural forces and a variety of physical limitations attending oil drainage, are responsible for the retention of 75 per cent or more of the original oil content of practically every oil deposit where wells are drilled. According to reliable authorities, actual recovery by ordinary methods of flowing and pumping is only from 10 to 25 per cent of the original oil content. The greater part of the oil retained is held within the sand pores by capillarity, and as a film completely enveloping each sand grain, the latter being due to the force of adhesion.

LESTER C UREN

In addition a large percentage of the original oil content probably remains in the sand by reason of the inadequacy or inefficiency of application of the expulsive forces. In the previous article of this series, it was shown that dissolved and occluded natural gas—the principal expulsive agent—is probably less than 10 per cent efficient in its application. The frictional resistance offered by minute sand pores to the movement of a viscous oil, is so great that the available expulsive forces are often inadequate to cause movement of the oil into a well at a commercially profitable rate.

Other forces active in expelling oil from the sands are also likely to be inefficient in their operation. For example, the hydrostatic pressure of edge-water often produces irregular flooding effects, leading to the trapping of large bodies of oil in fine-grained, lenticular oil sands that become surrounded by water-saturated sands of coarser texture. Gravitational drainage leaves large bodies of oil-saturated sands below the drainage slopes formed by the "angle of repose" of oil in the sand. A proper understanding of the forces and conditions which limit the efficiency of the expulsive forces is essential in the development and application of effective production methods.

Capillary Retention of Petroleum in Reservoir Rocks

Porous solids containing openings of capillary size exert an attraction contact to draw the liquid into the pore spaces. Examples of capillary action are common in every-day, familiar objects and operations, such as the absorption of ink by a blotter, the drying effect of a towel, and the rise of kerosene in the wick of a lamp or stove. In a similar way, by operation of capillary force, the pores of a sand or rock absorb oil, and the same force resists other forces which may later tend to expel the oil from the rock pores.

Rise of Oil in a Capillary Tube

CAPILLARITY results from the combined operation of several natural forces. The molecular attraction which exists between the oil and the mineral composing the reservoir sand, causes the oil to spread over the grain surfaces. The surface tension of the oil resists this extension of the oil surface, and cohesion prevents its disruption under the influence of the opposing forces. We may conveniently study the effects of these forces by considering their several functions when oil is caused to rise in a capillary tube. Consider the conditions sketched in Figure 1, for example.

A capillary tube, open at each end, is held in an upright position with the lower end immersed below the surface of oil in a beaker. The molecular attraction existing between the oil and the glass, of which the tube is composed, causes the oil to spread up the glass walls of the tube, above the surface of the fluid in the beaker. Along their line of contact, the oil curves upward against the glass as a result of this attractive force. The surface tension of the oil resists distention of its surface, and is powerful enough to lift a column of the oil in the tube. The cohesion of the liquid prevents the oil column from severing connection with the reservoir of oil below. The attraction of the glass for the oil is capable of drawing the oil upward indefinitely until limited by the ability of the surface tension of the liquid to support the oil column below. The column of oil thus gradually climbs in the tube until an equilibrium condition is reached.

If we assume, in Figure 1, that the system has come into equilibrium, and if

T is the surface tension of the oil in dynes per centimeter,

R is the radius of the tube in centimeters,

G is the density of the oil relative to pure water at 0°C.,

A is the acceleration of gravity in centimeters per second per second,

H is the capillary rise in centimeters, and

a is the angle of contact made by the oil against the glass surface, it can be shown that[1]:

$$H = \frac{2\ T \times \text{cosine}\ a}{A \times R \times G} \qquad \text{(1)}$$

Methods of Determining Surface Tension

FORMULA (1), above, indicates that the capillary rise is directly proportional to the surface tension of the oil, and inversely proportional to the oil

Influence of Back-Pressure on Recovery

READERS of this series of special articles by Prof. Uren, recognized authority on oil production practice, are fortunate in having given them the fundamental theories regarding natural forces affecting the flow of oil in the ground which underlie the present discussion on advisability of legislation to conserve gas in the ground in oil fields.

The Uren articles will give the oil man a better basis for discussing the issues presented through the introduction in Oklahoma of the bill to force operators to hold back-pressures on their wells.

With his next article Prof. Uren comes to the subject directly involved—the influence of back-pressures in securing increased efficiency in oil recovery. It is only in the last few years, through experiment and research work, that the oil industry has begun to learn the effect of natural gas dissolved in the oil on flow of oil in the ground.

New discoveries along this line are being continually made. The purpose of Prof. Uren, in this special series, is to keep the practical oil man, too busy to do the extended reading necessary to keep up with these new developments, informed upon new methods and new theories which are to come into practical use on oil producing properties.

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[1] Washburne, H. H., "Introduction to the Principles of Physical Chemistry." McGraw-Hill Book Co., 1916. See particularly pages 40-52.

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density. This relationship provides a convenient means for determining the surface tension of an oil, and measurement of the height of rise of oil in a capillary tube is one of the commonly used methods for estimating surface tension. Other methods requiring more elaborate apparatus involve the measurement of the force necessary to pull a wire ring of standard proportions up through the oil surface, or the determination of the weight of a drop of the fluid as formed under standard test conditions, on the tip of a pipette. The writer has found the du Nouy Tensiometer, which makes use of the ring method, a rapid and convenient means of making comparative tests on the surface tension of oils. The du Nouy instrument is illustrated in Figure 2.

The various methods for determining surface tension do not produce concordant results when applied to petroleum, probably because the tension of fluid mixtures is not constant, being influenced to an important degree by surface absorption, which slowly changes with time. The capillary tube method of measuring surface tension, which is slow in operation and gives ample time for the surface forces to reach equilibrium, gives consistently lower results than other methods. (See Table 1).

Surface Tension of Crude Petroleum

IN view of the fact that the magnitude of capillary force, and therefore, the extent of capillary retention of petroleum in reservoir rocks, is directly proportional to the surface tension of the oil, it will be of interest to compare the surface tensions of various crudes to see to what extent this property varies. Harvey[2] has conducted a series of tests on oils from many American fields with the aid of the du Nouy Tensiometer, and reports the values given in Table II.

A previous article of this series[3] has shown that, on account of the solution of large quantities of hydrocarbon gases at elevated pressure, the surface tension of crude petroleum increases as the pressure is increased. It is also known that surface tension decreases markedly as the temperature rises.

Capillary Attraction of Unconsolidated Sands for Crude Petroleum

IN considering the capillary attraction of porous reservoir rocks for oil, it is apparent, from the foregoing discussion, that the force exerted will depend primarily upon the size and shape of the sand pores and the surface tension and density of the oil. The first article of this series[3] presented data indicating the

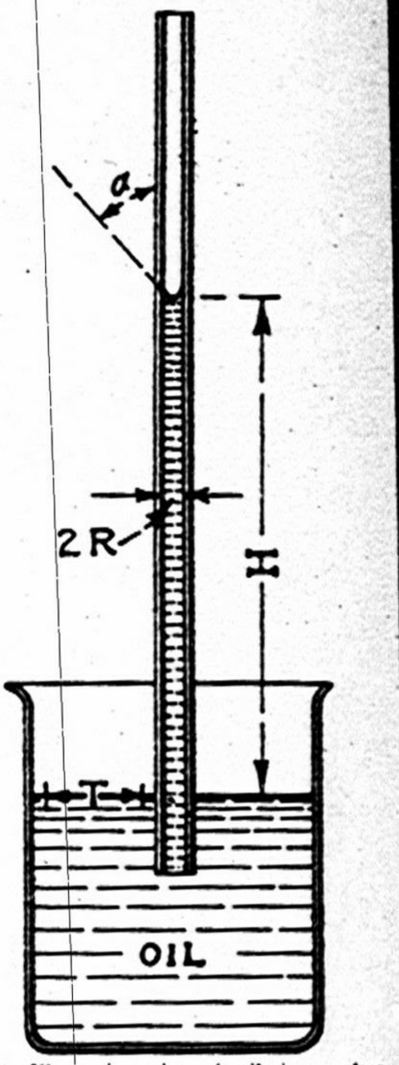

Fig. 1—Illustrating rise of oil in a glass capillary tube

probable size of the sand pores for different sizes of grains. It was there shown that both the porosity and grain size were instrumental in determining the size of the pore spaces between grains, and that even in sands as coarse as twenty mesh, the minimum cross-section of the pore spaces is only 0.035-sq. mm., or about 0.22-mm. in diameter.

It is known that capillarity is exerted by glass-walled tubes on water, only when the tubes have a diameter of less than 0.508-mm[4]. In the case of crude petroleum and silica sands, the maximum size of pore opening exerting capillary force is probably somewhat less than this, but the exact value is unknown. However, research conducted under the direction of the writer by Mr. A. H. El Diirawi[5], has indicated that un-

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[2] Harvey, E. H., "The Surface Tension of Crude Oils," Industrial & Engineering Chemistry, Vol. 17, January, 1925, p 85.

[3] See National Petroleum News, issue of January 19th 1927.

[4] Washburne, C. W., "Capillary Concentration of Gas and Oil," Transactions, Amer. Inst. Mining & Metall. Engrs., Vol. L, (1914), p. 831.

[5] El Difrawi, A. H. "A Quantitative Study of the Various Factors Influencing Gravity Drainage of Oil from Saturated Sands," a thesis for the degree of Master of Science, University of California, December, 1926.

Table 1—Comparison of *Surface Tension Measurements* by Various Methods[2]

Oil From	Surface Tension in Dynes as determined by: du Nouy Tensiometer	Capillary Tube	Drop-Weight Method
Madill Field, Oklahoma	26.8	23.9	25.6
Burkburnett Field, Texas	30.0	27.3	28.8
Alleghany County, New York	30.2	27.3	28.9
Augusta Field, Kansas	31.5	28.5	30.2
Corning Field, Ohio	30.5	27.5	29.8

consolidated sands coarser than thirty mesh do not, in general, display appreciable capillary attraction on crude petroleum, while sands of finer size do so.

Table II. Surface Tensions of Crude Petroleums from Various American Oil Fields as Determined with the Du Nouy Tensiometer[*]

State	Field	Surface Tension in Dynes/cm
Arkansas	El Dorano	30.2
California	Coalinga (East Side)	34.3
	Kern River	37.7
	Sunset	35.7
	Santa Maria	31.5
	Montebello	35.6
Kansas	Augusta	31.5
	Florence	31.2
Indiana	Lima	30.9
Illinois	Lawrence	30.9
Kentucky	Ragland	32.9
Louisiana	Caddo	30.5
	Pine Island	34.3
Montana	Winnett	27.4
New York	Alleghany County	30.2
Ohio	Lima	30.9
	Corning	30.5
Oklahoma	Billings	29.8
	Ponca	30.2
	Cushing	29.8
	Hewitt	31.2
Pennsylvania	Mercer County	32.9
	Alleghany County	28.8
Texas	Burkburnett	30.0
	Humble	34.6
	Goose Creek	33.6
	Media	31.2
	Somerset	29.1
	West Columbia	32.6
Wyoming	Big Muddy	32.2
	Salt Creek	34.3

[*] Note: All measurements were made at a temperature of 24°C

The capillary force developed was also found to vary with the sand porosity which, as has been previously pointed out, is jointly responsible with the size of sand grain, in determining the size of the sand pores. The magnitude of capillarity increases as the size of grain and porosity decrease.

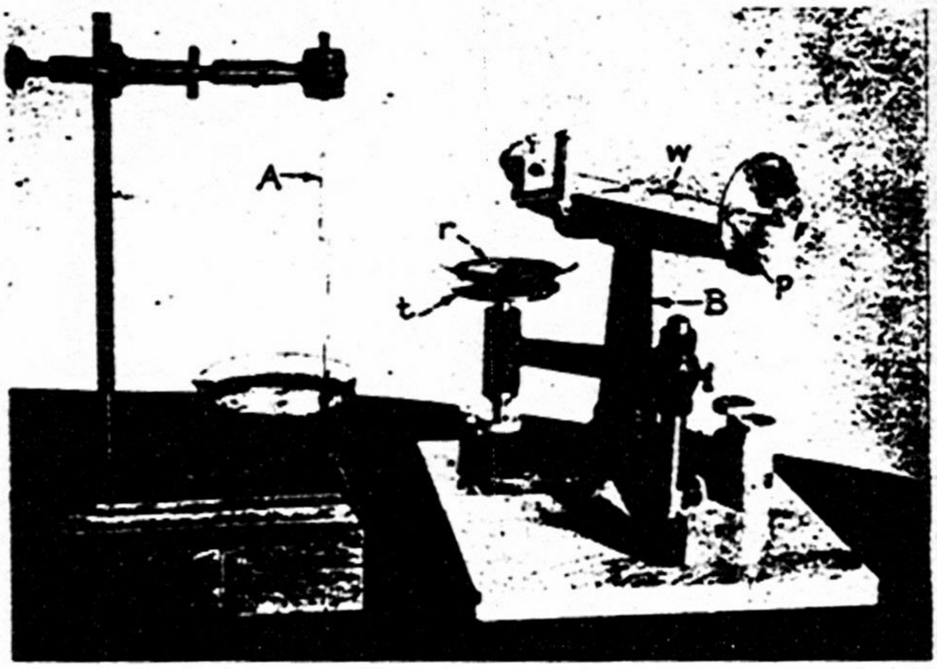

Fig. 2—Apparatus for measuring the surface tension of oils. A—Capillary tube; B—Du Nouy Tensionmeter; R—Platinum wire ring; W—Torsion wire; T—Adjustable table for supporting oil container; P—Recording pointer and graduated dial

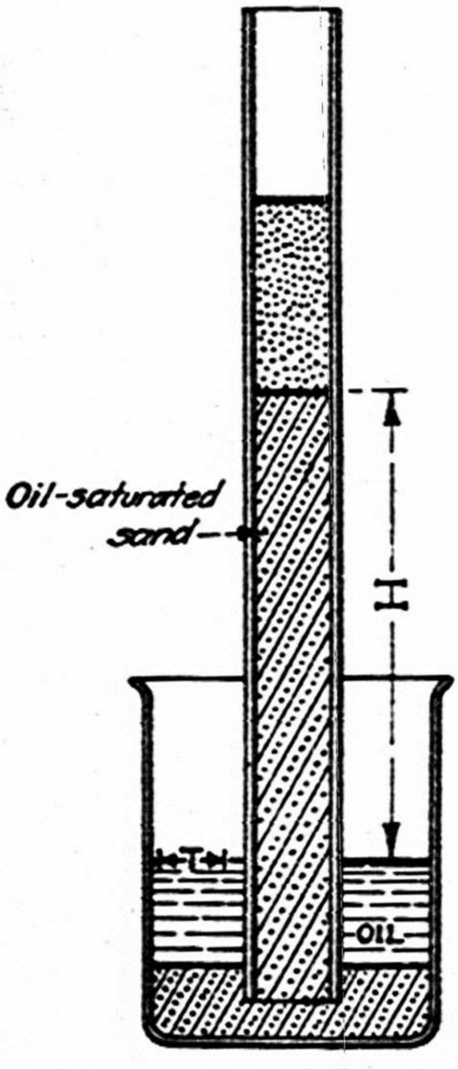

Fig. 3—Apparatus used in measuring capillary rise of oil in sand

In an effort to determine quantitatively, the magnitude of capillary force in rock pores of various sizes, El Difrawi performed a series of experiments in which the capillary rise of crude petroleum in accurately sized, unconsolidated sands of known porosity, was determined.[*] Screened sands of various sizes, ranging from 20 to 70 mesh, were compacted in glass tubes to various porosities and the sand-filled tubes supported in a vertical position with their lower ends immersed in a reservoir filled with crude oil of known surface tension, density and viscosity. (See Figure 3). After the oil drawn up into the sand by capillary force had reached an equilibrium position, the height of capillary rise of oil in the sand above the surface of oil in the reservoir was measured. From the data so secured, the following empirical formula was derived:

$$H = \frac{275 \times T \times \text{cosine } a}{G \times P^{\text{[illegible]}} \times D} \quad \ldots\ldots (2)$$

In this formula,

H is the capillary rise in inches,

T is the surface tension in dynes per centimeter,

a is the angle of contract between the oil and the mineral composing the grains of sand,

G is the specific gravity of the oil,

P is the porosity of the sand in per cent, and

D is the mean diameter of the sand grains in millimeters.

This formula permits of some interesting deductions and applications. It shows, for example, that porosity is the most important factor in determining the magnitude of capillary force. The surface tension and specific gravity of the oil and the size of the sand grains are factors of lesser importance than porosity. The investigation also indicated that the viscosity of the oil is not a factor in determining the magnitude of capillary retention.

In discussing gravitational drainage of oil from sand, in the previous article of this series, it was explained how a zone of oil-saturated sand in the bottom of the productive stratum, is left undrained by normal processes of recovery. This layer of undrained sand is composed of two parts: that below the "angle of repose," which contains oil beyond the influence of gravitational drainage, and that above, comprising a body of sand which was described as the "zone of capillary retention," a zone which remains saturated with oil by operation of capillary force.[*]

The thickness of the zone of capillary retention is equivalent to the height to which the oil would rise in the sand under the influence of capillary force, and may, therefore, be computed with the aid of formula (2) given above. Applying the formula, for example, to an oil having a surface tension of 25-dynes per centimeter (measured by capillary tube method), and a specific gravity of 0.95, in a sand having a porosity of 20 per cent and an average grain size of 0.2-mm., we find that the capillary rise, H, is 36.8-inches. These are not abnormal values, and the result of the computation indicates that a zone of sand three feet thick is left saturated with oil, held by the force of capillarity after all normal drainage ceases.

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[*] Uren, L. C. and El Difrawi, A. H., "Capillary Retention of Petroleum in Unconsolidated Sands," Transactions, Amer. Inst. Mining & Metall. Engrs., Feb. 1927.

[*] See Figure 6 of the second article of this series, National Petroleum News, January 26, 1927.

Similar computations for oils of comparatively high surface tension, low density, and for sands of very low porosity and small grain size, show that in extreme conditions the zone of capillary retention may be as much as 15-feet thick. This means that in an oil sand 30 feet thick, as little as half of it may be productive of oil, the remainder being within the zone of capillary retention, in which the oil is permanently held beyond the influence of natural drainage forces.

Where an oil-producing zone comprising several component sands separated by impervious "partings" of clay or shale, is drained, each impervious barrier in the formation will be the base for such a zone of capillary retention. (See Figure 4.) The aggregate volume of oil so retained by capillarity may under such conditions be a large percentage of the original oil content.

Retention of Crude Petroleum in Reservoir Sands by Adhesion

OILS are attracted to most mineral substances by an intermolecular force of considerable intensity. Once brought into contact with the oil, the latter will spread over the mineral surface until the oil is reduced to an exceedingly thin film, or until the available mineral surface is completely engulfed. Of course in an oil sand, every particle of mineral surface is exposed directly to the oil and each grain becomes completely enclosed with an encasing film. When an oil sand is in process of drainage, after all free-draining oil has escaped and the sand pores have become evacuated of oil to such extent as may be permitted by capillarity, the sand grains still remain wet with oil. The adhesive film forms an enclosing envelope which completely surrounds each sand grain, a film held to the mineral surface by intermolecular attraction. This film persists because of the cohesive force existing between the oil molecules, which resists disruption of the oil film.

but rather, as a zone of finite thickness in which the molecules of the liquid interlock, or become "rooted" into those of the solid mineral.[7] There is good evidence indicating that most apparently solid surfaces have, in reality, a loose molecular structure that readily permits fluids to enter. Quartz, marble, porcelain and other minerals are easily stained by oil, and the stain is not merely a surface coating, but extends to measurable depths.

Sand that has been in contact with oil feels "greasy," though the surface oil may have been completely removed by solvents; and if subsequently brought into contact with oil, the mineral will greedily retain it. On the other hand, it cannot be readily wet with water. It seems probable that the sub-surface pores of the mineral may retain a fluid, even though the surface is apparently free of it.

The writer has made microscopic studies of broken fragments of pebbles of various minerals which were previously coated with a thin film of oil, the surplus oil being permitted to drain away and the film to become practically dry by contact with air before the pebbles were broken. Under the microscope, the minute "roots" of the oil film extending into the mineral surface, are clearly visible, varying in depth and character with the crystalline texture of the mineral.

IT should be understood that sand grains though small in size, are nevertheless frequently capable of being broken into much smaller fragments, and the minute cleavage planes and fractures along which such subdivision may occur, communicate directly with the grain surfaces. These minute crevices exert capillary force and often draw oil from the grain surfaces into the very heart of the crystalline structure. Grains of quartz, limestone, feldspar, mica, hornblende and other common sand-forming minerals, all display this tendency, and evidence of it is apparent on crushing sand grains and examining the fragments under the microscope. (See Figure 5).

The writer has performed a series of tests designed to indicate the quantity of oil that may be retained on and within sand grains in this way. In these tests, small pieces of various common sand-forming minerals, about an inch in diameter, were ground to smooth surfaces of geometrical form so that their surface areas could be closely estimated by actual measurement. The specimens thus prepared, were carefully weighed and then dipped in crude petroleum. On removal from the oil, the surplus fluid was permitted to drain away from the specimens by supporting them for ten minutes on pin points. The specimens were then again weighed, and the increase in weight due to the retained oil, determined.

KNOWING the density of the oil and the surface areas exposed to the oil, the volume of oil per unit of exposed mineral surface was then computed. Assuming that the oil retained was distributed on and within the mineral surface in a layer of uniform thickness, the computed thickness of the oil coatings varied with the viscosity of the oil and with the smoothness and texture of the mineral surfaces, but ranged between 0.04-mm. and 0.18-mm., the former volume being obtained for Santa Fe Springs, 31° California crude on quartz, and the latter for 15° Kern River, California, crude on hornblende.

It is interesting to compute the volume of oil that would be thus retained on and within the grain surfaces in sands of various mesh. In the first article of this series,* the writer has given estimated values for the surface areas presented by sand grains of different mesh, per cubic foot of sand. It was shown, for example, that a cubic foot of 28-mesh sand presents a grain surface of 2166 square feet to the oil. If we assume that the oil coating left on and within the grain surface is 0.05-mm. thick, the total volume of oil so re-

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[7] Bulman, H. L., "A Contribution to the Study of Flotation," Transactions, Institution of Mining & Metallurgy (London), Vol. XXIX (1919-20), p. 44-204.

*See January 19, 1927 issue of National Petroleum News.

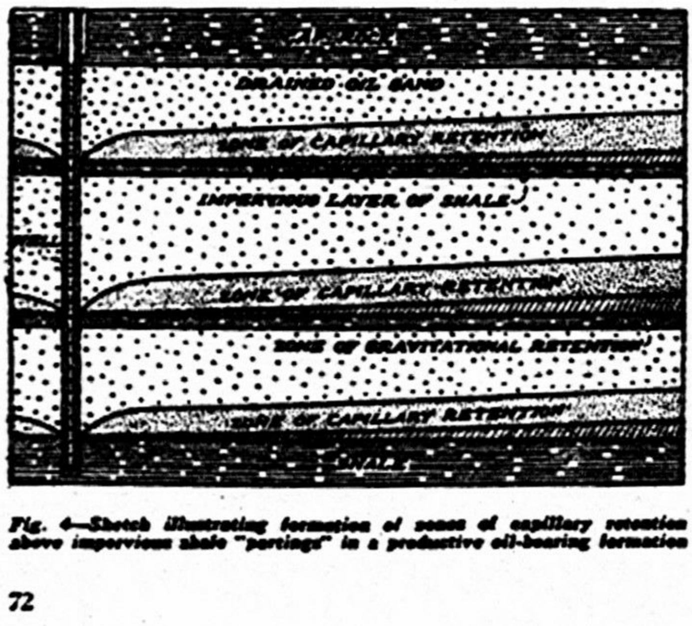

SHALE
DRAINED OIL SAND
ZONE OF CAPILLARY RETENTION
IMPERVIOUS LAYER OF SHALE
ZONE OF CAPILLARY RETENTION
ZONE OF GRAVITATIONAL RETENTION
ZONE OF CAPILLARY RETENTION
SHALE

Fig. 4—Sketch illustrating formation of zones of capillary retention above impervious shale "partings" in a productive oil-bearing formation

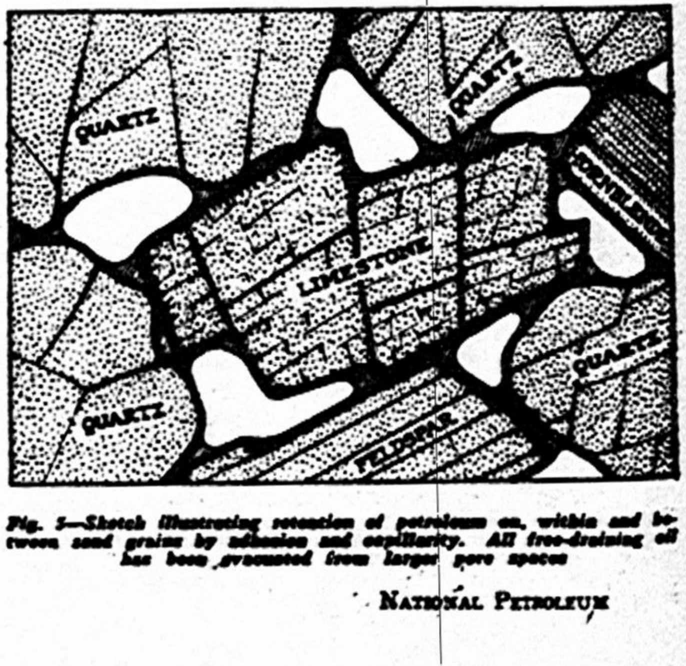
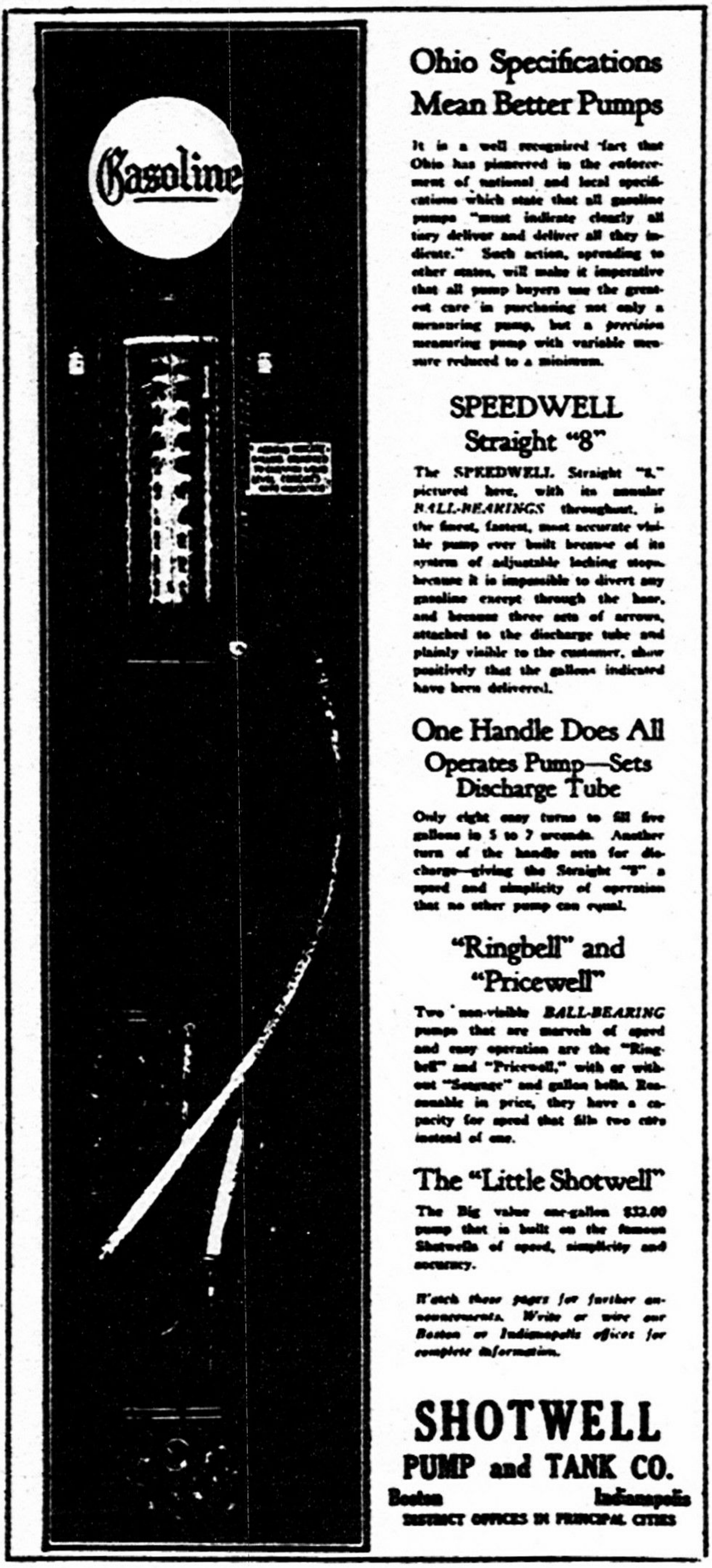


Fig. 5—Sketch illustrating retention of petroleum on, within and between sand grains by adhesion and capillarity. All free-draining oil has been evacuated from larger pore spaces



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tained on a cubic foot of sand, would be 0.34-cubic ft. Finer grained sands, presenting a greater surface to the oil, would retain a still greater quantity. A forty-eight mesh sand, for example, would be capable of retaining 0.69-cu. ft. of oil per cubic foot of reservoir sand. It should be noted that oil so retained on and within the sand grains, is not producible by ordinary methods of recovery. It is a component of the oil content of the sand that is separate and distinct from that stored within the pores between sand grains, from which we derive our producible oil.

Hardy and Nottage developed a method for measuring the adhesive force between lubricating oils and mineral substances, and have determined relative values for various oils and mineral substances.[8] It is reported that the adhesive force varies with the character of the mineral substance, but for any given substance, is directly proportional to the molecular weight of the oil, and decreases in a straight-line relationship with temperature.

Resistance to Flow of Oil Through Reservoir Sands

IN the previous article of this series, it was shown that the drainage system of a well assumes the form of a multitude of pore channels, radiating outward through the reservoir sand in all directions from the well as a center. Oil and gas move through these channels toward the well in the form of minute gas bubbles alternating with slender filaments of oil. Irrespective of the character of the expelling force, whether it be expanding gas, hydrostatic pressure or gravitational force, movement of the fluids is resisted by: (a) friction of the oil and gas on the rock material forming the walls of the channels; (b) internal friction of the oil in overcoming its viscosity; (c) the resistance offered by the gas bubbles to deformation in passing through restrictions in the flow channel; and (d) the capillary drag of the minute openings through which the oil must pass.

Considering that pressure is applied in varying degree throughout the entire length of each drainage channel, and that energy is consumed in so many different ways in accomplishing movement of the oil, accurate determination of the resistance to flow becomes a most complex problem. Indeed, no formula has yet been devised which adequately expresses the relationship of all of the variables influencing flow resistance; nor does one seem worth striving for, since the irregularities of geologic structure and lithologic texture would seem to defeat the practical application of mathematical principles.

It is nevertheless of interest to formulate the variables influencing oil flow through the reservoir rock, if only to develop the relationships existing between them. A notable effort toward this end has been made by King[9] and

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[8] Hardy, W., and Nottage, M., "Studies in Adhesion," Proceedings of the Royal Society of London, Vol. 112A, p. 62-74 (1926).

D is the effective diameter of the sand grains in millimeters,

O is the percentage porosity,

L is the radius of drainage of the well in feet,

R is the radius of the well through the productive sand, in feet, and

C is a constant.

It should perhaps, be pointed out, that these equations are applicable only to conditions in which the oil is "dead," that is, without occluded gas bubbles. They do not include the additional pressure losses resulting from the distortion of gas bubbles and in overcoming capillary "drag."

While such formulae are of doubtful practical utility, they are nevertheless of value in demonstrating the relative effects of the several variables on oil flow. For example, formula (4) shows that the flow of oil from the reservoir sand into a well varies:

(a) Directly as the effective pressure,

(b) Directly as the thickness of the productive sand,

(c) Directly as the square of the mean diameter of the sand grains,

(d) Directly as the three and three-tenths power of the sand porosity,

(e) Inversely as the absolute viscosity of the oil, and

(f) Inversely as the logarithm of the value of the ratio of the drainage radius of the well to the radius of the well. This is equivalent to saying that the rate of production of the well decreases as the distance over which the oil is to be moved increases, and increases as the diameter of the well increases.[33]

No discussion of the mathematical and physical principles governing the flow of oil through sands would be complete, without reference to the work of Mr. S. C. Herald. We have already had occasion to refer to some of Mr. Herald's conclusions, but the writer again wishes to call the attention of the reader to the wealth of material relating to our present topic that is embodied in Mr. Herald's articles.[34]

Rate of Oil Flow Varies with Distance From the Well

CONSIDERATION of formula (5), covering channel flow, shows that the pressure loss—which is a measure of the sand resistance—is directly proportional to the rate of flow; and with a given rate of flow, doubling the pressure doubles L, the length of the sand column, or the distance over which the oil will flow. When we consider radial flow on the other hand, such as is characteristic of oil flow through a reservoir sand toward a well, it is apparent that a very different condition exists. The rate of flow through the flow channels is not constant, but increases as the well is approached. Different flow channels impinge upon each other and merge, necessitating more rapid movement of the fluids near the walls of the well than at remote points.

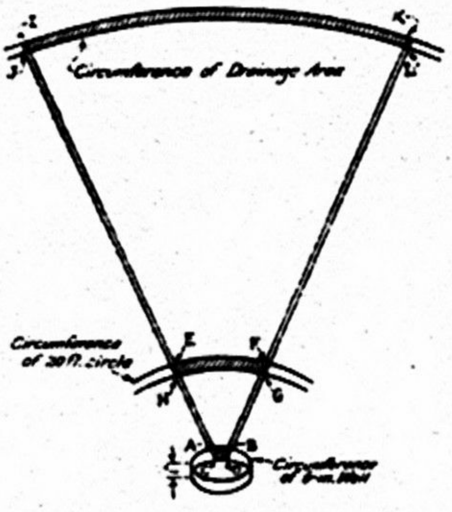
I
J
K
L
Circumference of Drainage Area
Circumference of 20 ft. circle
E
F
H
G
A
B
Circumference of 6-in. Well

Fig. 6—Horizontal wedge-shaped segment of drainage area of a well, illustrating increase of flow cross-section with distance from the well

The writer has shown that the rate of flow of the oil in the reservoir sand varies inversely as its distance from the axis of the well.[33] Consideration of the Figure 6 will demonstrate the essential truth of this statement. In this figure, a horizontal, wedge-shaped segment of the drainage area of a well is shown. Let it be assumed that the well is six inches in diameter, and that it is effective in drawing oil from a circular area 600-feet in diameter, with the well as its center. Let it be assumed that the area ABCD, intercepted by the segment on the walls of the well, is one-inch square. It is apparent that the area EFGH intercepted by the same segment on a cylinder 20-feet in diameter, having the axis of the well as a center, would be forty times as large; that is, it would intercept an area of 40-square inches.

Since approximately the same quantity of oil must flow through each cross-section, it is clear that the oil is flowing forty times as fast at the wall of the well as it is at a distance of ten feet from the well axis, and the pressure loss would vary proportionately. In section IJKL, on the circumference of the drainage area, the area intercepted by the segment is 1200-square inches, and the flow is theoretically zero. Because of the extremely low velocities of flow in the outer half of the drainage area, the pressure loss is negligible.

Figure 7, developed with the aid of formula (4), shows that the greater part of the pressure loss in moving oil through the reservoir sand to a well is lost within ten feet of the walls of the well. This results from the greater velocity of the oil in the vicinity of the well. Knowledge of this fact suggests that, if we could be content with a lower rate of recovery and were to restrain the rate of flow of oil through the sands, the wells would drain larger areas and would ultimately produce a greater quantity of oil. Producing oil through the neck of a funnel is a very inefficient process at best, but if we must do it in this way, restriction of the rate of flow should increase the efficiency of recovery.

Conclusion

THIS article presents the principal known facts concerning the forces which are responsible for the retention of petroleum in reservoir rocks. The mode of operation and effects of capillarity, grain adhesion and sand friction in limiting the rate of oil flow and efficiency of recovery, have been briefly explained. This paper, together with the first two articles of this series, concludes a brief study of the factors influencing the drainage of oil from reservoir rocks into wells, insofar as they have been disclosed by recent literature and research. The topics discussed in these three articles are of fundamental importance in determining appropriate methods of well control and operation, and in devising and applying more efficient methods of oil recovery; topics with which we shall be concerned in later articles of this series.

The next paper, which will deal with the influence of back-pressure in securing increased efficiency in oil recovery, will appear in an early issue of National Petroleum News.

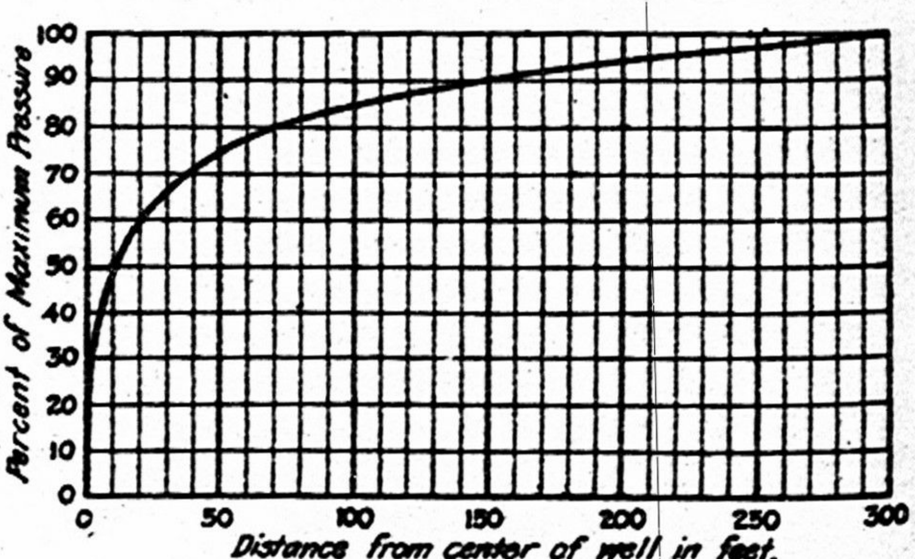

Fig. 7—Graph showing pressure loss of oil flowing through sand into a well over a drainage radius of 300 feet

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[33] Uren, L. C., "Increasing the Production of Petroleum by Increasing the Diameter of Wells," Trans., Amer. Inst. Mining & Metall. Engrs., Feb., 1924.

[34] Herald, S. C. An extended series of articles extending through the 1925-6-7 issues of the Oil and Gas Journal.

Pl. Ex. F

Effect of Dissolved Gas upon the Viscosity and Surface Tension of Crude Oil

By C. E. Beecher[*] and I. P. Parkhurst,[*] Bartlesville, Okla.

In the course of the experimental and development work of Henry L. Doherty in an endeavor to obtain an increased yield of oil from oil-bearing sands, it was Mr. Doherty's claim and contention that oil in an undisturbed pool was different in character and behavior than the same oil when raised to the surface of the earth, and that the gas dissolved in the oil caused a marked reduction in its viscosity and surface tension. Prior to 1924 no information to support this contention could be found in the literature or by a discussion of the subject with technical men in Government and private laboratories. So far as could be ascertained no experimental work had been carried on to indicate that Mr. Doherty's claim was either right or wrong. All parties consulted agreed that the viscosity of the oil would be affected by gas dissolved therein to the extent that natural gasoline was present in the gas, but so far as could be determined any additional effect of the natural gas was unknown.

Accordingly, it was necessary to devise equipment and carry on experiments which would either prove or disprove Mr. Doherty's contention or claim. Such apparatus was built under Mr. Doherty's direction and experiments were carried on to determine definitely the viscosity and the surface tension of the crude oils which contain dissolved gases under different pressures. The results of the experimental work carried on have proved that the claim and contention of Mr. Doherty were correct in every particular, as will be seen from the discussion of the subject and the data contained in this paper.

REDUCTION OF VISCOSITY BY DISSOLVED GAS

At a pressure of 500 lb., and a temperature of 70° F., it was found that a natural gas such as is associated with the oil would reduce the viscosity about 50 per cent. when a given crude oil was saturated with the gas. Increasing the pressure another 500 lb. could not be expected to reduce the viscosity the remaining 50 per cent. However, some reduction in viscosity would take place as indicated by the curves showing the relation between pressure and relative viscosity. Pressures of 1800 lb. may exist at depths around 4100 ft. and at present a large amount of oil is being produced from much greater depths. Under such pressures sufficient gas might dissolve in the oil to make the viscosity almost equal to that of kerosene.

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[*] Production engineers, Empire Gas & Fuel Co.

Viscosity is the most important physical quality of oil which retards its flow through a pipe line or through the small irregular openings of the average oil sand; therefore, if some method of producing oil can be devised such that a major portion of the gas will remain in solution and the oil retain its fluidity it is possible that the volume of oil recovered from the sands can be greatly increased.

Reduction of Surface Tension

The surface tension of crude oil is reduced by dissolved gas. The results of experiments with two different crude oils saturated with gas at pressures from 400 to 500 lb. indicate a reduction of approximately 20 per cent. in the surface tension of the oils.

Many of the small openings in an oil sand are of capillary size and hold a large percentage of the oil which is not recovered by present production methods. As the dissolved gas escapes from the oil the surface tension increases and likewise the capillary force which holds the oil within the sand. We are not prepared to say that surface tension is the only factor that holds the 80 per cent. of the original oil in the sands. If, however, surface tension should be the only force and if by keeping the gas in solution the surface tension could be reduced by 20 per cent. then we might expect an 80 per cent. greater ultimate recovery from the sands.

A great volume of oil must flow through the sands at a rapid rate and for some distance to account for the large production of some wells. The expulsive force of natural gas dissolved in and associated with the oil, the rock pressure, the reduction in viscosity due to increased earth temperatures and other factors do not alone offer an explanation of the large gusher wells. It is believed that the flow of oil through the sands in such large volumes is only possible because of the reduced viscosity and surface tension of the oil resulting from the gas in solution.

It is the purpose of this paper to give some of the results obtained from the experimental work on the solubility of gas in oil under pressure and the changes in the viscosity and surface tension of the oil. The authors wish to acknowledge the many helpful suggestions offered by A. W. Ambrose and Robert G. Griswold.

Method and Apparatus for Determining Solubility of Gases in Oils

The apparatus used for determining the amount of gas dissolved in oil under pressure is shown in Fig. 1. It consisted essentially of a large cent. methane, while in curve 2, the methane content of the gas was 82.5 per cent.

All analyses of natural gas referred to in this paper were made by the combustion of the gas in an atmosphere of oxygen. The results, therefore, do not represent the true amount of methane and ethane present, but do show whether the light or heavy hydrocarbons tend to predominate.

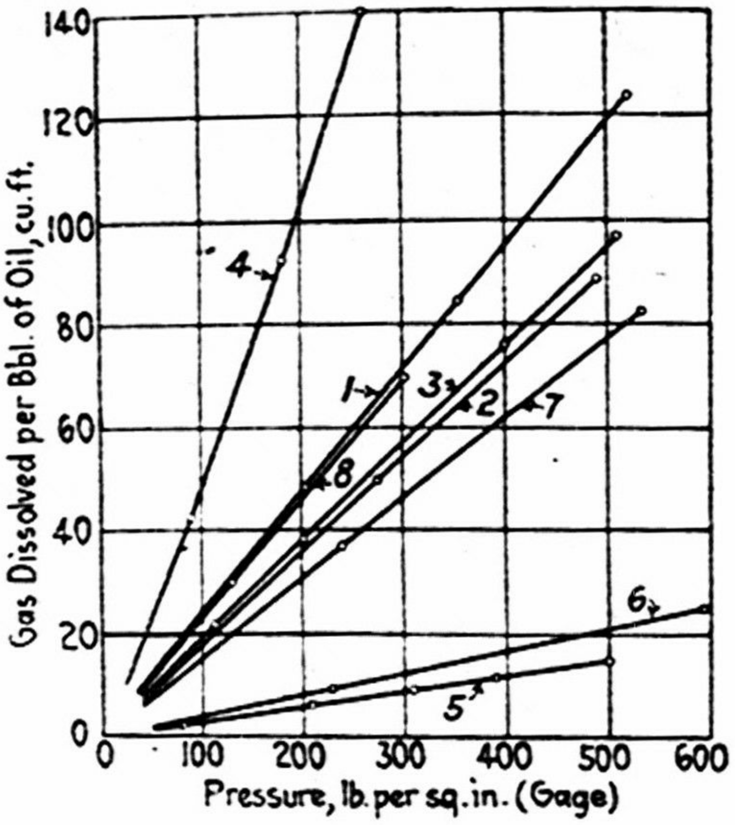

FIG. 2.—SOLUBILITY OF VARIOUS GASES IN CRUDE OILS UNDER PRESSURE AT 70° F.

Curve 1. Natural gas No. 1 in Oklahoma crude oil.—35.4° A. P. I.
Curve 2. Natural gas No. 2 in Oklahoma crude oil.—35.4° A. P. I.
Curve 3. Natural gas No. 1 in Oklahoma crude oil.—30.2° A. P. I.
Curve 4. Carbon dioxide in Oklahoma crude oil.—30.2° A. P. I.
Curve 5. Hydrogen in Oklahoma crude oil.—30.2° A. P. I.
Curve 6. Air in Oklahoma crude oil.—30.2° A. P. I.
Curve 7. Natural gas No. 2 in Oklahoma crude oil.—30.2° A. P. I.
Curve 8. Natural gas No. 2 in Bradford crude oil.—44.3° A. P. I.

ANALYSES OF GASES

	No. 1 PER CENT.	No. 2 PER CENT.
CH_4	52.0	82.5
C_2H_6	39.0	5.5
CO_2	1.2	5.9
O_2	0.4	0.3
Residue	7.4	5.8

For any given gas, the volume that will be dissolved depends upon the character of the crude oil, if other conditions are constant. The lighter gravity oils dissolve more gas than the heavier oils. This is illustrated by curves 1 and 3, Fig. 2. These curves show a difference in solubility of approximately 20 per cent. for the same gas in oils of 35.4 and 30.2° A. P. I., respectively. As a further example, curves 7 and 8 show a difference of approximately 32 per cent. in the solubility of the same gas in two different oils.

SOLUBILITY OF OTHER GASES IN CRUDE OILS

A few experiments were conducted to determine the solubility of gases such as carbon dioxide, hydrogen and air in crude oils. Carbon dioxide was found to be more soluble than natural gas, while hydrogen and air are only slightly soluble, the hydrogen being less soluble than the air. Curves 4, 5, 6 and 7 in Fig. 2, show the relation between the pressure and the volume of gas dissolved in the same crude oil for carbon dioxide, hydrogen, air and a dry natural gas, respectively.

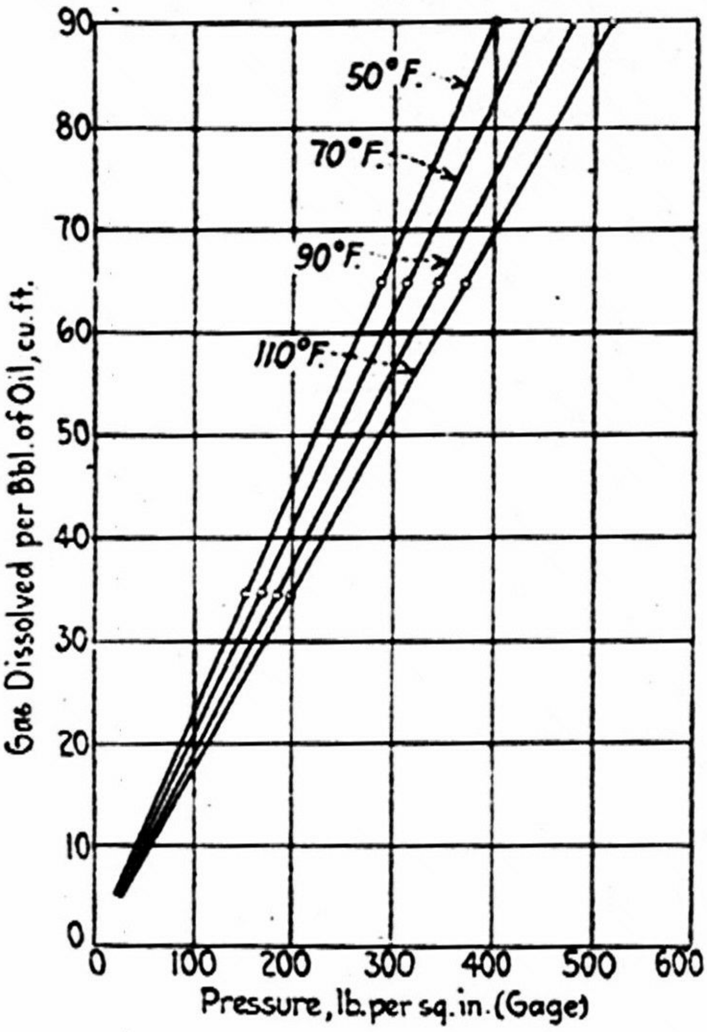

FIG. 3.—SOLUBILITY OF NATURAL GAS IN A CRUDE OIL AT DIFFERENT TEMPERATURES.

For this particular oil the gas was found to be approximately four times as soluble as air, but only one-third as soluble as carbon dioxide. A similar ratio will probably apply to other crude oils.

Since the experiments referred to in this paper were completed, Dow[1] and Calkin have conducted a series of experiments to determine the solubility of a practically pure methane gas and of air in various crude and refined oils. The results of their work sustain those given in this paper.

ROCK PRESSURE AND VOLUME OF DISSOLVED GAS

Rock pressures of 1000 lb. per sq. in. or greater, are not uncommon in many oil fields, and at such pressures, the volume of gas dissolved in the oil should be at least twice as great as that obtained from the laboratory experiments with pressures around 500 lb. per sq. in. Table 1 has been prepared to show the cubic feet of gas dissolved in a barrel of oil at pressures from 300 to 1000 lb. per sq. in.

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[1] D. B. Dow and L. P. Calkin: Solubility and Effects of Natural Gas and Air in Crude Oil. *Rpt. of Investigations*, Bur. Mines, Ser. No. 2732 (Feb., 1926).

TABLE 1.—*Cubic Feet of Gas Dissolved in a Barrel of Oil at Different Pressures*

Gage Pressure Lb./Sq. In.	Oklahoma Crude 30.2° A. P. I.				Oklahoma Crude 35.4° A. P. I.	
	Gas No. 1	Gas No. 2	Air	CO_2	Gas No. 1	Gas No. 2
300	57.0	46.5	12.3	161	71	54
500	95.0	77.5	20.5	276	118	90
1000	190.0	155.0	41.0	563	236	180

Note.—See Fig. 2 for analyses of gases.

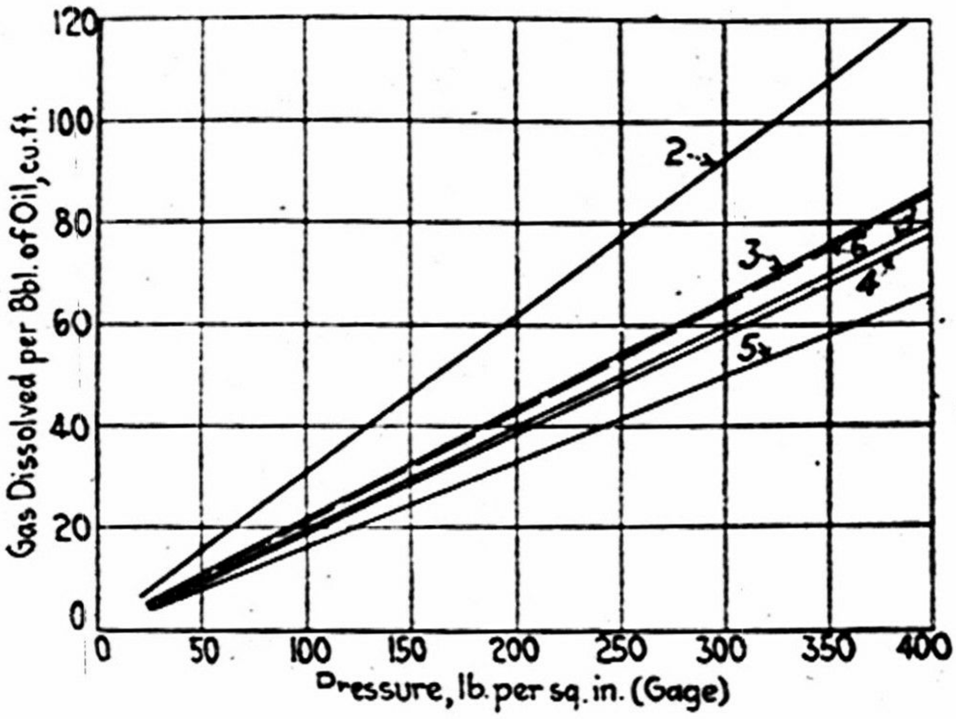

FIG. 1.—SOLUBILITY OF NATURAL GAS IN AN OKLAHOMA CRUDE OIL (36.6° A. P. I.) AND IN ITS REFINED PRODUCTS AT 76° F.

ANALYSIS OF GAS

Curve 1. Crude oil.
Curve 2. Gasoline.
Curve 3. Kerosene.
Curve 4. ~~Gas oil.~~
Curve 5. Fuel oil.
Curve 6. Composite curve.

	PER CENT.
CH_4	82.5
C_2H_6	5.5
CO_2	5.9
O_2	0.3
Residue	5.8

EFFECT OF TEMPERATURE ON SOLUBILITY OF GAS IN OIL

Other conditions remaining constant, the quantity of gas that will dissolve in oil depends upon the temperature. The relation between pressure and the volume of natural gas dissolved in a crude oil at various temperatures from 50 to 110° F. is shown by the curves in Fig. 3. As the temperature increases the amount of gas that can be dissolved in the oil decreases, but even at the higher temperatures, large quantities of gas other products. This experiment again demonstrates that natural gas is more soluble in the lighter oils.

APPARATUS FOR DETERMINING VISCOSITY OF CRUDE OIL CONTAINING DISSOLVED GAS

The viscosity of crude oil is commonly determined by the Saybolt viscosimeter. This apparatus, however, is not designed to measure viscosity under pressures other than atmospheric; therefore, to determine the viscosity of oils containing dissolved gas under pressure, it was necessary to construct a viscosimeter that would operate under high pressures. Fig. 5 shows the details of the pressure viscosimeter used. It was operated in the following manner:

Note

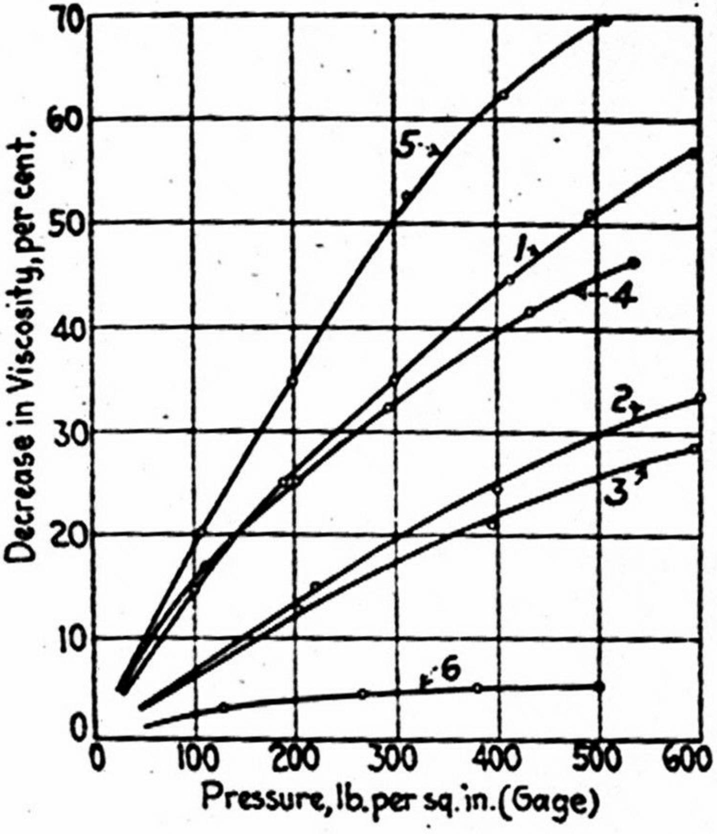

FIG. 6.—DIAGRAM SHOWING DECREASE IN VISCOSITY OF CRUDE OILS CONTAINING GASES DISSOLVED UNDER PRESSURE.

Curve 1. Natural gas No. 1 in Oklahoma crude oil.—30.2° A. P. I.
Curve 2. Natural gas No. 2 in Oklahoma crude oil.—30.2° A. P. I.
Curve 3. Natural gas No. 2 in Oklahoma crude oil—35.4° A. P. I.
Curve 4. Natural gas No. 1 in Oklahoma crude oil.—35.4° A. P. I.
Curve 5. Carbon dioxide in Oklahoma crude oil.—30.2° A. P. I.
Curve 6. Hydrogen in Oklahoma crude oil.—30.2° A. P. I.

ANALYSES OF GASES

	No. 1 PER CENT.	No. 2 PER CENT.
CH_4	52.0	82.5
C_2H_6	39.0	5.5
CO_2	1.2	5.9
O_2	0.4	0.3
Residue	7.4	5.8

A fixed quantity of oil was placed in the apparatus through valve F, then gas was troduced under pressure through the same valve, and the apparatus agitated unti c oil was completely saturated. The ′ mperature was controlled by means of a constant temperature bath in which the entire apparatus was placed. To obtain the viscosity the apparatus was inverted until the oil had drained into chamber *A* through tube *B*. It was then inverted and the oil in chamber *A* started to flow through capillary tube *C* into the bottom chamber. The time required for the fluid level to rise from mark *D* on the lower gage glass to mark *E* on the upper glass was taken. This time can be converted into Saybolt seconds by means of a calibration curve giving the relation between the Saybolt time and the pressure-viscosimeter time.

By means of tube *B* the pressure is equalized throughout the apparatus. This tube is much larger than the capillary tube *C* and thus permits the oil to flow readily into chamber *A* when the viscosimeter is inverted. Capillary tube *C* is 1/16-in. diameter and 2 in. long, and is drilled through a solid piece of brass as shown in the detail sketch in Fig. 5.

EFFECT OF DISSOLVED GAS ON VISCOSITY OF CRUDE OIL

The viscosity of crude oil is greatly reduced when the oil contains gas in solution. The decrease in viscosity depends upon the amount of gas dissolved in the oil if other conditions are constant. An oil with high initial viscosity will show a greater relative decrease for a given amount of dissolved gas than one with a lower initial viscosity.

Fig. 6 shows the relation between pressure at which various oils were saturated with various gases and the percentage decrease in viscosity of the oil. The viscosity decreases with an increase in pressure because more gas is dissolved at the higher pressure. Curves 1 and 2 are for the same oil but with a different gas in solution; the same is also true of curves 3 and 4. Under the identical conditions, the gas dissolved in the oils as shown by curves 1 and 4 is more soluble than the gas dissolved in the oils for curves 2 and 3, and therefore at the same pressure produced a greater reduction in the viscosity of the oils.

Curves 2 and 3 indicate the reduction in viscosity that resulted when the same gas was dissolved in the different oils. The gas is more soluble in the oil for curve 3 than in the oil for curve 2, but the reduction in viscosity is less. The initial absolute viscosity of the oil for curve 2 is approximately 3½ times greater than that for the oil of curve 3.

Curves 5 and 6 show the reduction in viscosity when carbon dioxide and hydrogen, respectively, are dissolved in the same oil. Carbon dioxide is extremely soluble and therefore produced the greatest reduction in viscosity at a given pressure.

Effect of Dissolved Air

An effort was made to determine the effect of dissolved air upon the viscosity of an oil. The results were not consistent. In some tests the viscosity was slightly reduced and in others, increased. The increased viscosity may be due to oxidation of the oil when in contact with the air.

Dow and Calkin[2] found that the viscosity of two oils with which they experimented was increased when containing air in solution and in one were made with the oil saturated with various amounts of gas. The relative surface tension was determined by the height to which the oil would rise in the capillary tube. The absolute surface tension was determined by calibrating the capillary tube with a liquid of known surface tension.

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[2] D. B. Dow and L. P. Calkin: *Op. cit.*

EFFECT OF DISSOLVED GAS ON THE SURFACE TENSION OF CRUDE OIL

The surface tension of crude oil is reduced by dissolved gas. Fig. 9 shows the relation between the volume of gas dissolved in two different oils and the surface tension in dynes per cm. These curves are approximately parallel. The difference appears to be caused by a variation in the initial surface tension. The relation between percentage reduction in surface tension and the volume of dissolved gas for both oils is shown by the one curve in Fig. 10. This indicates that equal volumes of the same gas dissolved in each oil caused the same relative decrease in surface tension. Insufficient information is available to justify drawing any such conclusion.

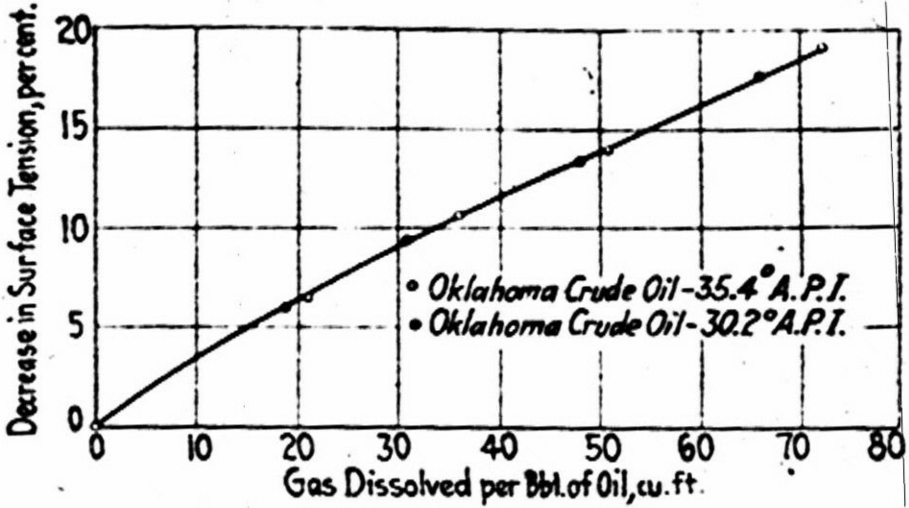

FIG. 10.—DIAGRAM SHOWING DECREASE IN SURFACE TENSION OF CRUDE OILS CONTAINING NATURAL GAS DISSOLVED UNDER PRESSURE (COMPOSITE CURVE).

RELATION BETWEEN SURFACE TENSION AND RECOVERABLE OIL

A large percentage of oil which present production methods fail to remove from the sands is held by capillarity. As the gas dissolved in the oil escapes, the surface tension is increased and, likewise, the capillary force which is a measure of the surface tension. If this increase in surface tension could be prevented during the process of extracting oil from the sands, a greater volume of oil should be recovered

DISCUSSION

J. R. McWilliams,[*] Tulsa, Okla. (written discussion).—Those of you who are not acquainted with the meaning of the terms "critical velocity," "viscous flow," and "turbulent flow," I would like to refer to Prof. L. C. Uren's book, "Petroleum Production Engineering," Chap. 18, p. 545.

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[*] Petroleum engineer, Skelly Oil Co.

Plffs Ex

R. I. 3035
September, 1930.

REPORT OF INVESTIGATIONS

DEPARTMENT OF COMMERCE -- BUREAU OF MINES

THE RECOVERY OF OIL FROM SANDS BY THE "GAS DRIVE"[1]

By

Joseph Chalmers[2], I. H. Nelson[3], and D. B. Taliaferro[4],

Table 4. - Solubility of pressure media in oil used

Pressure medium	Solubility			
	25 lbs. per sq. in. gage		50 lbs. per sq. in. gage	
Helium	0.3	cu. ft. per bbl.	0.7	cu. ft. per bbl.
Air	1.5	do	3.0	do
Dry gas	4.7	do	9.5	do
Propane-dry gas mixture	17.0	do	34.0	do
Propane	157.2	do	407.0	do

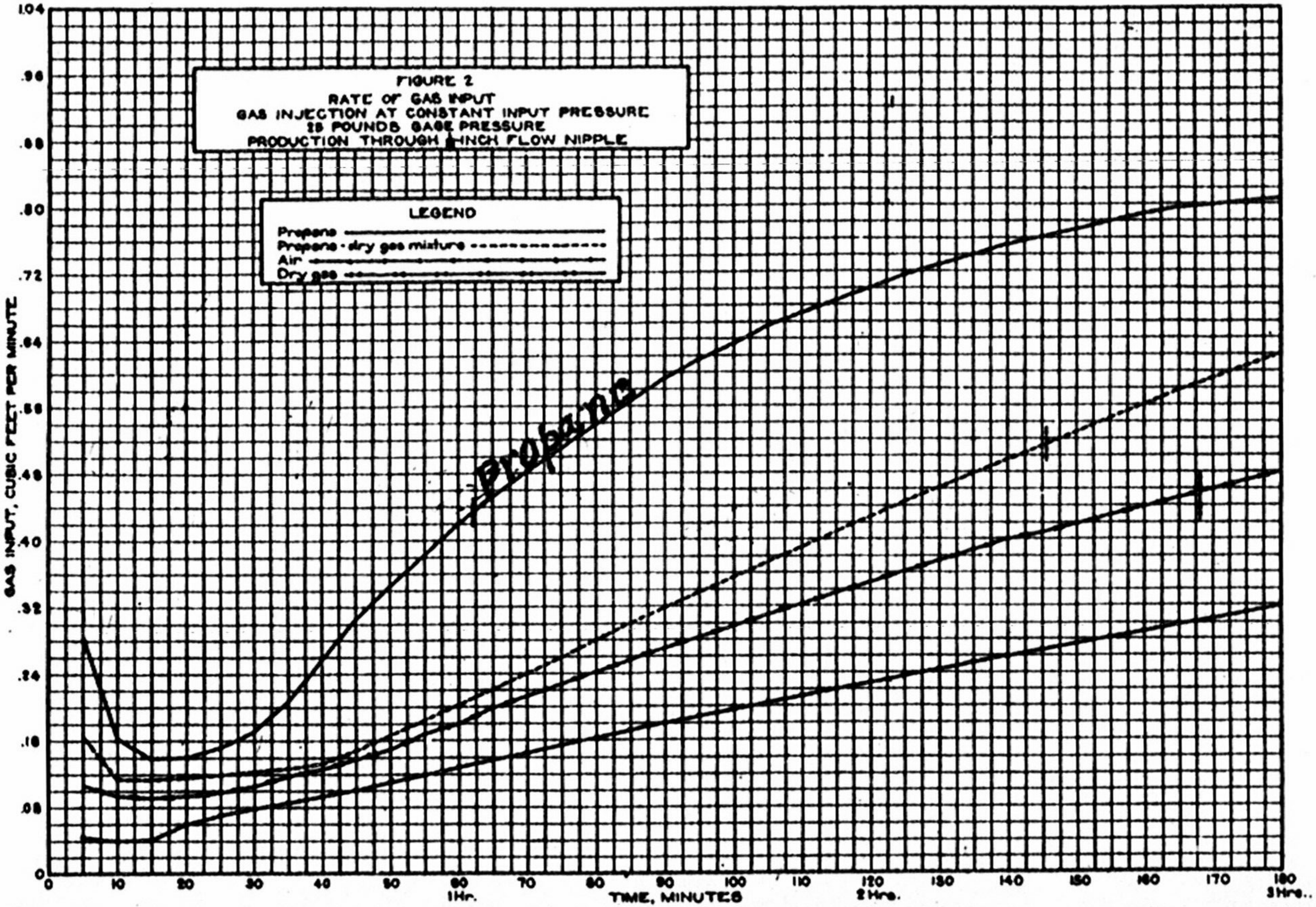

FIGURE 2
RATE OF GAS INPUT
GAS INJECTION AT CONSTANT INPUT PRESSURE
25 POUNDS GAGE PRESSURE
PRODUCTION THROUGH [illegible] INCH FLOW NIPPLE

NOTE:- The distinctive vertical lines through the curves indicate the times at which 22% of the original oil content of the sand was recovered by gas injection using the different pressure media. The time necessary for air was 190 minutes which is beyond the range of the chart

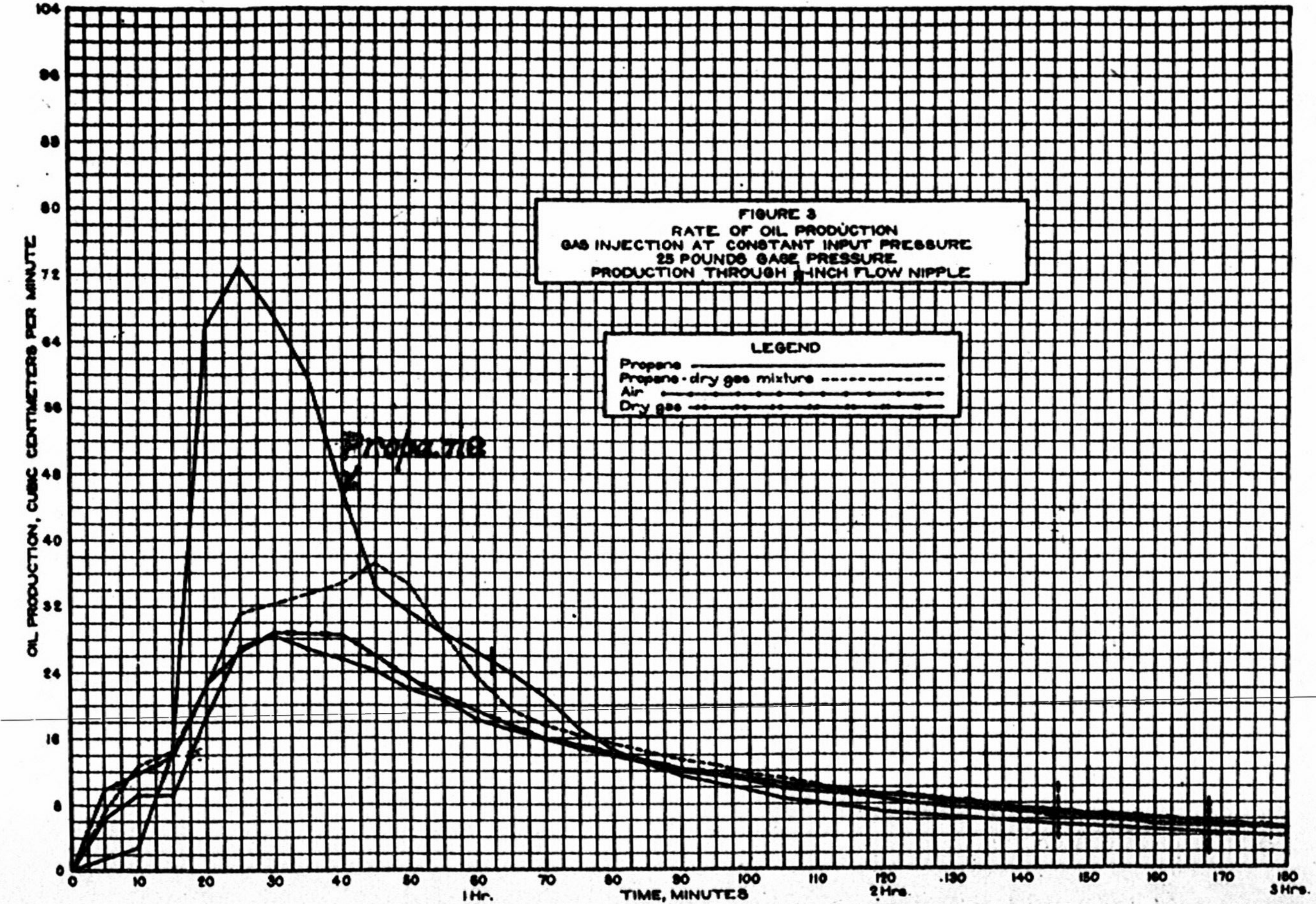

FIGURE 3
RATE OF OIL PRODUCTION
GAS INJECTION AT CONSTANT INPUT PRESSURE
25 POUNDS GAGE PRESSURE
PRODUCTION THROUGH ¼ INCH FLOW NIPPLE

NOTE:- The distinctive vertical lines through the curves indicate the times at which 22%

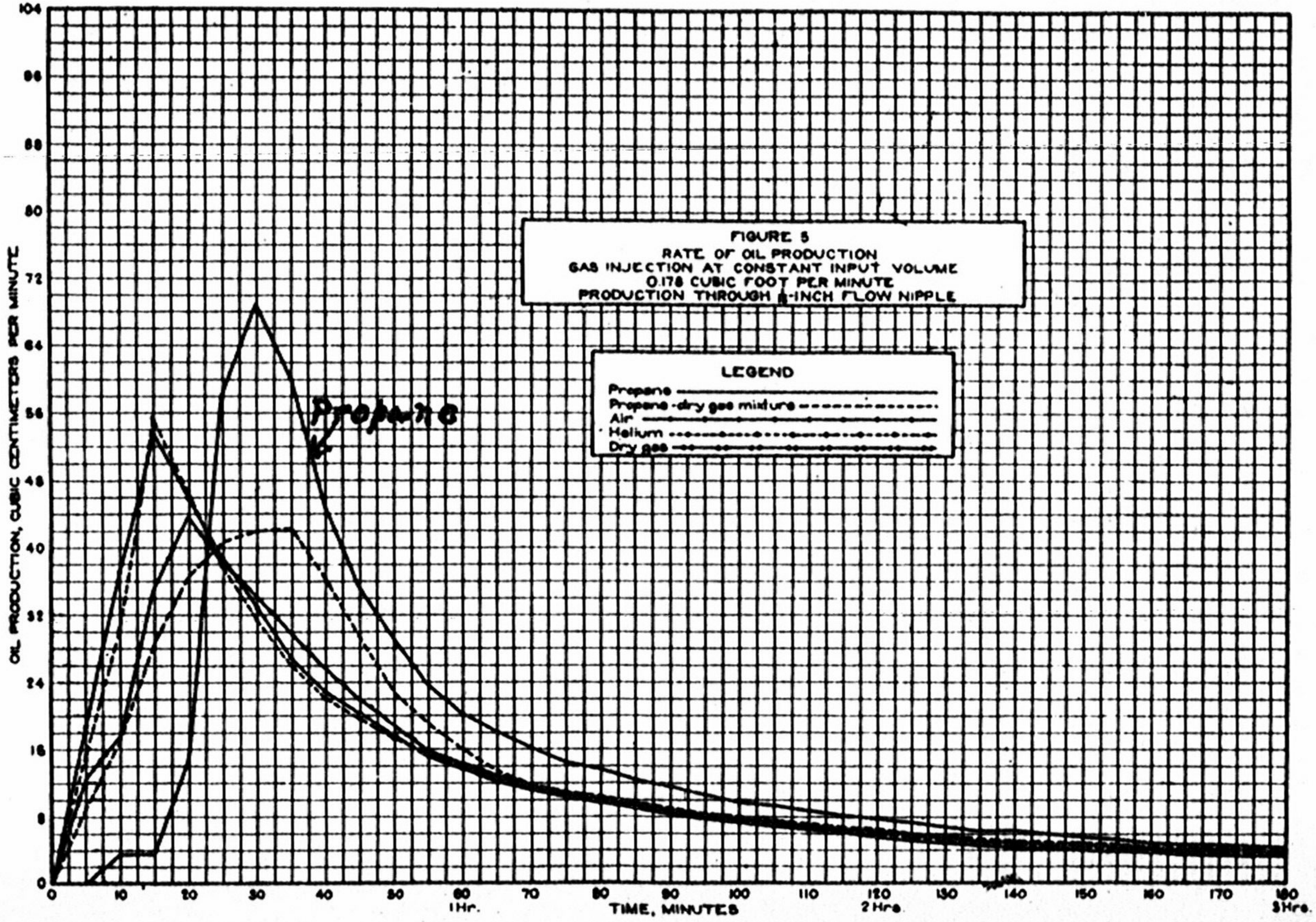

FIGURE 5
RATE OF OIL PRODUCTION
GAS INJECTION AT CONSTANT INPUT VOLUME
0.178 CUBIC FOOT PER MINUTE
PRODUCTION THROUGH [illegible]-INCH FLOW NIPPLE

R. I. 3035

Table 5. - Comparison of propulsive effects of different gases injected at constant pressure 1.

PRESSURE MEDIUM	Specific Gravity	Oil recovered by "natural flow," per cent	Time interval to recover additional 22 per cent of oil by gas injection, minutes	Total volume of gas required to recover 22 per cent of oil by gas injection, cu. ft.	Total Gas-oil ratio for gas injection	Mean flow-tube pressures, Pounds Gage Input	Mean flow-tube pressures, Pounds Gage Output	Work done to recover 22 per cent of oil by gas injection, foot-pounds
Propane	1.523	23.3	62	15.431	1,067	25.0	5.8	21,124
Propane-dry gas mixture	1.000	23.2	146	37.758	2,610	25.0	5.3	54,302
Air	1.000	23.2	190	37.851	2,577	25.0	3.5	60,959
Dry gas	.690	23.4	168	44.269	3,060	25.0	4.7	66,167

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[1] The data in this table apply to a gas injection pressure of 25 pounds per square inch gage. The oil and gas were produced through a 1/16-inch flow nipple.

Table 6. - Comparison of propulsive effects of different gases injected at constant rate [1]

PRESSURE MEDIUM	Specific gravity	Oil Recovered by "natural flow", per cent	Time interval to recover additional 22 per cent of oil by gas injection, minutes	Total volume of gas required to recover 22 per cent of oil by gas injection cu. ft.	Total gas-oil ratio for gas injection	Mean Flow-tube pressures, pounds gage		Work done to recover 22 per cent of oil by gas injection, foot-pounds
						Input	Output	
Propane	1.523	23.2	96	17.088	1,161	17.78	3.13	20,400
Propane dry gas mixture	1.000	23.2	132	23.496	1,624	19.97	3.04	32,800
Air	1.000	23.4	130	23.140	1,600	25.55	3.10	38,800
Helium	0.138	23.4	138	24.564	1,698	23.54	2.75	39,700
Dry gas	0.690	23.5	163	30.082	2,080	13.97	2.55	41,900

[1] The data in this table apply to a gas injection rate of 0.178 cu. ft. per minute. The oil and gas were produced through a 1/16-inch flow nipple.

6I

Pl. Ex I.

Solubility of Natural Gas in Crude Oil

Preliminary Report on Investigation of the Bureau of Mines Determining These Values for Oil and Gas From Natural Reservoir

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Petroleum engineers generally are familiar with the investigations of Dow and Reistle, Beecher and Parkhurst, and Dow and Calkin relative to the solubility of natural gas in crude oil. Since the publication of the results of those investigations and the work of Mills and Heithecker, little additional knowledge on this interesting and important subject has appeared in the petroleum engineering literature.

The reports of Beecher and Parkhurst and Dow and Calkin agree substantially. The data from both investigations showed that, under the conditions of the tests, the solubility of natural gas in crude oil increased in direct proportion to the pressure at which the gas was put into solution, and the solubility decreased to a considerable extent with increased temperature. These facts, and others relating to the changes in viscosity, surface tension and specific gravity of the crude caused by the solution of gas in the oil, have been given due consideration in the petroleum industry, and the recognition of these facts has resulted in a great improvement in the technique of producing oil.

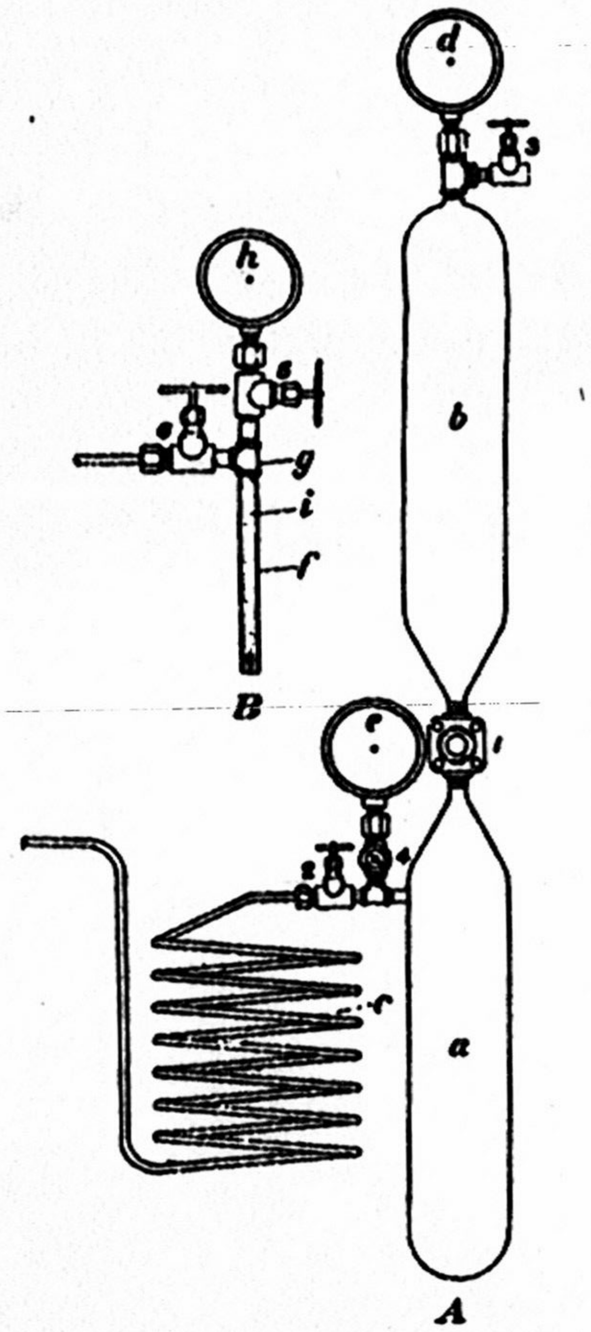

Figure 1—High-pressure sampling apparatus. Separator "B" replaces "b" in laboratory operations.

A—High pressure sampling apparatus. B—The separator. Replaces b in laboratory apparatus. a—Lower sampling bomb 3½"x15". b—Upper sampling bomb 3½"x15". c—Copper coil leading from high pressure connection at well head, to a .¼" O.D. d—Pressure gauge. Determines pressure of sample. e—Auxiliary pressure gauge. Indicates leaks after sampling. f—Hydraulic nipple ½"x6". g—Hydraulic tee ½". h—Pressure gauge. Indicates pressure when dissolved gas is liberated. i—BB shot used as packing in separator. 1—Lubricated high pressure stop cock ½". 2—Inlet. Forged steel needle valve ¼". 3—Outlet. Forged steel needle valve ¼". 4—Needle valve. Forged steel ¼". 5—Needle valve. Forged steel ¼". 6—Separator outlet. Needle valve. Forged steel ¼".

However, in these first experiments, various grades and types of weathered crude oil were contacted at various pressures up to 500 pounds per square inch gauge with gases deficient to a considerable degree in the heavier hydrocarbons, as compared with the gas that was originally in solution in the oil in its natural underground reservoir. The amount of dissolved gas that was liberated upon reducing the pressure to 1 atmosphere was measured. For these reasons, the complete significance of the effect of dissolved gases in crude oil, as it occurs in nature, cannot be determined directly from the data obtained under the conditions of the test as described.

In the present investigation, well-head samples were obtained in suitable bombs at existing well-head pressure from flowing wells, and the amount of gas that was liberated upon gradual reduction of pressure was measured and analyzed. Samples under a pressure as high as 1,586 pounds per square inch absolute were obtained

Difference in Data

The difference in data obtained under the two general sets of conditions can be shown best by the following comparisons: Beecher and Parkhurst found that weathered Bradford crude of 44.8° A.P.I. gravity dissolved 70 cubic feet of dry natural gas per barrel of oil when the two substances were contacted under pressure up to 300 pounds per square inch gauge. The author, working with Kettleman Hills crude of 44.5° A.P.I. gravity, found that a well-head sample liberated 275 cubic feet of dissolved gas when the pressure was reduced through a corresponding pressure range. The difference of 205 cubic feet between the results of the two studies cannot be attributed to the fact that one crude was from California and the other from Pennsylvania, but rather to the different methods, as explained, which were employed in making the determinations.

In the application of experimental data obtained from weathered oil and dry natural gas, there is no doubt that the results of calculations reflecting the changes in the physical properties of natural oil-gas mixtures have been correct in trend, but it now appears that the numerical values of these calculations may have fallen short in magnitude. The fact that live oil obtained at the well-head contained greater quantities of dissolved gas than oil that had been in storage for some time was indicated to the author by his experiments on Burbank crude, which showed that .78 cubic feet of gas per barrel of oil were liberated from solution in the oil when the pressure was reduced from 2 pounds per square inch gauge to 26 inch vacuum; a reduction in absolute pressure of about 15 pounds, giving a final pressure of about one-tenth the original pressure. On the other hand, Dow and Calkin found that it required 378 pounds per square inch, or about 27 times their original pressure (which was atmospheric) to dissolve the same quantity of dry natural gas per barrel of weathered Oklahoma crude, which had a gravity of 31° A.P.I.

These great differences in the volume of gas that is in solution naturally in crude oil, as compared with the volume of gas that will dissolve in weathered oil when it is contacted with dry natural gas at high pressures artificially, indicate that many fundamental data regarding the solubility of gas in oil in the natural state are yet to be obtained.

This preliminary paper gives the major findings of a study of the Bureau of Mines which is being made to obtain data on the physical and chemical characteristics of natural oil-gas mixtures. By proper interpretation, it is believed that these data will indicate true solubility conditions in natural reservoirs.

Apparatus and Procedure

Figure 1A shows two high-pressure bombs connected by a half-inch lubricated stopcock (1). These bombs are forged from 3-inch double extra heavy seamless tubing. Their outside and inside diameters are approximately 3½ and 2¼-inch, respectively. The wall thickness, therefore, is approximately five-eighths inch. The length of each bomb is about 15 inches and the capacity of the lower bomb (a) including the port of stopcock (1) is approximately 705 cubic centimeters. All parts of the apparatus were tested to 2,500 pounds per square inch hydraulic pressure. Valve (2) connected at the side of bomb (a) is the inlet valve and valve (3) at the top of the upper bomb (b) is the outlet. These are forged steel needle valves. Valve (2) is connected to a coil of quarter-inch copper tubing (c) that leads to the connection at the well head. The assembled bombs and copper tubing are placed in a 70° F. water bath, and the apparatus is then subjected to the well pressure by opening valve (2). After examining the apparatus carefully for leaks, valve (3) is opened slightly, and, with lubricated stopcock (1) connecting the two bombs open, the oil and gas flow through the copper coil and the bombs at well-head pressure under flowing conditions. The oil drops to the bottom of bomb (a) and the gas discharges from the top of the upper bomb (b). This operation is continued until oil discharges with the gas from needle valve (3). After the oil has discharged from the top of needle valve (3) for about 10 minutes, this valve and also the inlet or lower needle valve (2) are closed, the copper tube is disconnected and the assembled bombs are allowed to remain in the 70° F. bath for 15 or 20 minutes, thereby allowing any gas bubbles that may be adhering to the walls of the bottom bomb to pass upward through stopcock (1) and rise to the top of the upper bomb. During this stabilizing process, the lower bomb is vigorously hammered at frequent intervals in order to jar loose any gas bubbles which may have adhered to the sides of the lower bomb.

Pressure gauge (d) indicates the pressure at which the sample is taken. Pressure gauge (e) is for the purpose of indicating leaks that may be present after the sample is obtained. Thus during the sampling operation, valve (4) is closed and remains closed until the sampling is complete. At that time, valve (1) is closed and valve (4) is opened. Leaks in the apparatus become apparent by a more or less continuous pressure drop, as indicated by gauge (e). Gauge (e) was highly important in the experiments at the Oklahoma City Field, where a number of samples were taken at one time, packed in ice and transported to Bartlesville, Okla., a distance of 200 miles, where they were placed in cold storage for periods varying from a few days to two or three weeks before the gas was drawn off into measuring bottles. In the California work, however, only one sample was taken at a time, and as bombs (a) and (b) were allowed to remain assembled during the short period of transportation from well to laboratory, any pressure drop that might occur could be readily observed on gauge (d). Consequently, under these conditions, there was no advantage in using gauge (e).

In preparing the apparatus and the

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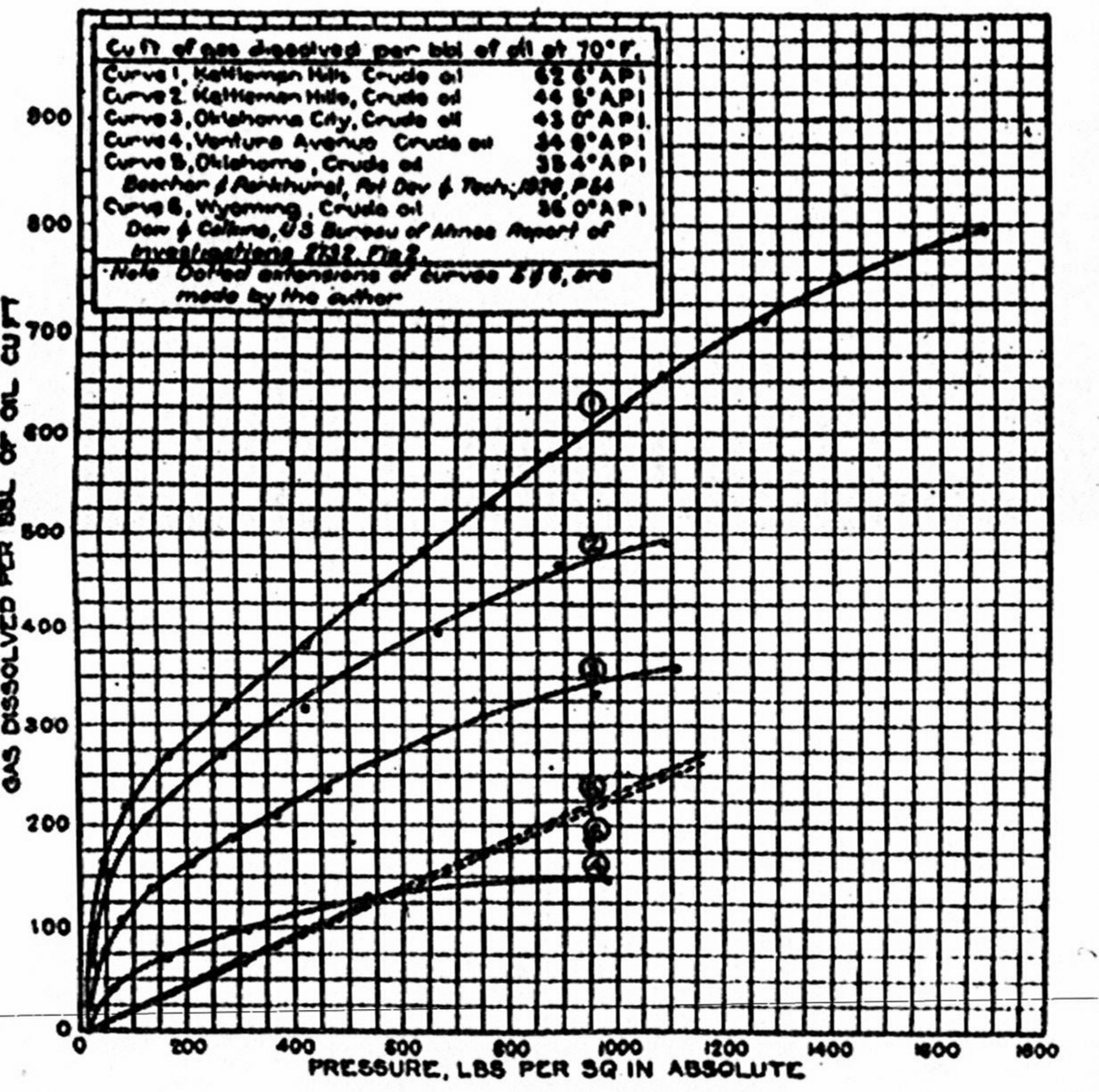

Figure 2—Solubility curves of various crude oils.

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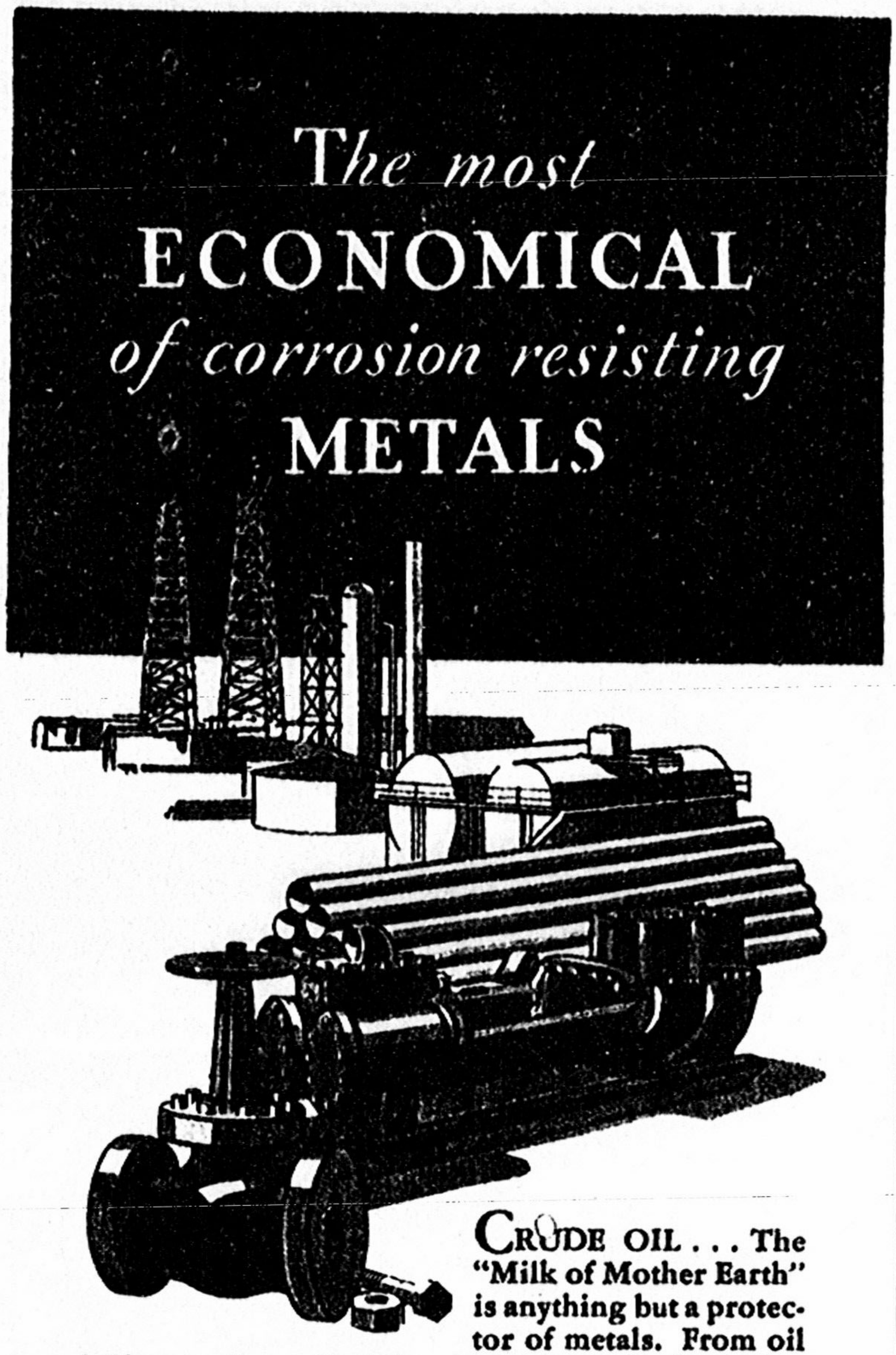

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gas-saturated sample for the subsequent laboratory work, the pressure is released from bomb (b), and its contents are discarded. The purpose of the upper bomb is to provide a means of completely filling the lower bomb with gas-saturated oil, without any free gas. At this stage of the operation, bomb (a) is ready to be prepared for drawing off the gas from the gas-saturated oil.

Field Laboratory Apparatus and Procedure

The upper bomb (b) is replaced by an assembly (Figure 1B) called the "separator." This assembly consists of a hydraulic nipple (f), ½x6 inches, a half-inch hydraulic tee (g), and needle valves (5) and (6), which are screwed into the top of the side outlets respectively of the tee. Pressure gauge (h) of suitable range is screwed into needle valve (5), and the needle valve (6) on the side outlet of the tee serves as the outlet for the gas coming out of solution as the pressure is released from bomb (a). The tee (g) and the nipple (f) are full of BB shot to reduce the space and to knock down any oil that may have a tendency to "foam up" into the separator from the lower bomb. While unscrewing the top bomb and replacing it with the separator, the temperature of bomb (a) is kept below 70° F. by means of an ice pack. After assembling, the separator and bomb are placed in a 70° F. bath, and the air in the separator assembly and in gauge (h) is exhausted by means of a vacuum pump; this evacuation was accounted for in subsequent measurements and calculations. Valve (6) is then closed, and stopcock (1), connecting the separator and bomb (a), is opened gradually; allowing the pressure to build up in the separator as slowly as possible. In the experiment represented by curve (1), Figure 2, the pressure in the bomb was reduced from 1,672 to 1,396 pounds per square inch during the first operation of releasing gas from bomb (a) to the separator. It took about 15 or 20 minutes for this pressure to become stabilized at the lower pressure. Throughout the period the bomb was hammered repeatedly. After the pressure became constant, gauge (h) was read, stopcock (1) was closed and the gas in the separator was drawn off slowly through rubber tubing connecting outlet needle valve (6) to calibrated 1-gallon bottles which had previously been filled with water. The gas in the calibrated measuring bottles and in the separator and tubing was brought to atmospheric pressure by means of a leveling bottle, and the volume of the gas liberated for each pressure drop was determined. At each gas-volume reading, the barometric pressure and the atmospheric temperature were recorded. It was assumed that the temperature of the gas in the bottles was the same as that of the atmosphere. The procedure of releasing gas from solution in the oil by stabilizing the pressure within the separator and bomb (a) and then collecting and measuring the gas contained in the separator, by manipulating valves (1) and (6), was repeated until the pressure in the bomb was reduced to atmospheric pressure. Upon opening the stopcock the second time (curve 1, Figure 2), the pressure stabilized at 1,263 pounds per square inch absolute, and the third opening reduced it to 1,070 pounds. As the pressure in the bomb was reduced, the procedure necessarily was changed. At lower pressures the volume of the separator and the gauge was not sufficient to produce a gas sample of suitable volume for complete analysis, as had been the case in the upper range of pressure. Therefore, to obtain a sample of sufficient volume for each successive pressure drop in the lower range, gas was drawn off slowly into the measuring bottles for a considerable time under control of valve (6) with stopcock (1) open. Before taking final observations on the sample being drawn, however, valve (6) was closed. With the closing of valve (6), pressure within the closed-in system built up, as indicated by consecutive readings on gauge (h). The closed-in system was then allowed to stabilize. Stabilization was accelerated by violently hammering the bomb. This hammering also had the effect of preventing a supersaturated condition of the oil in bomb (a). When the pressure became stabilized, stopcock

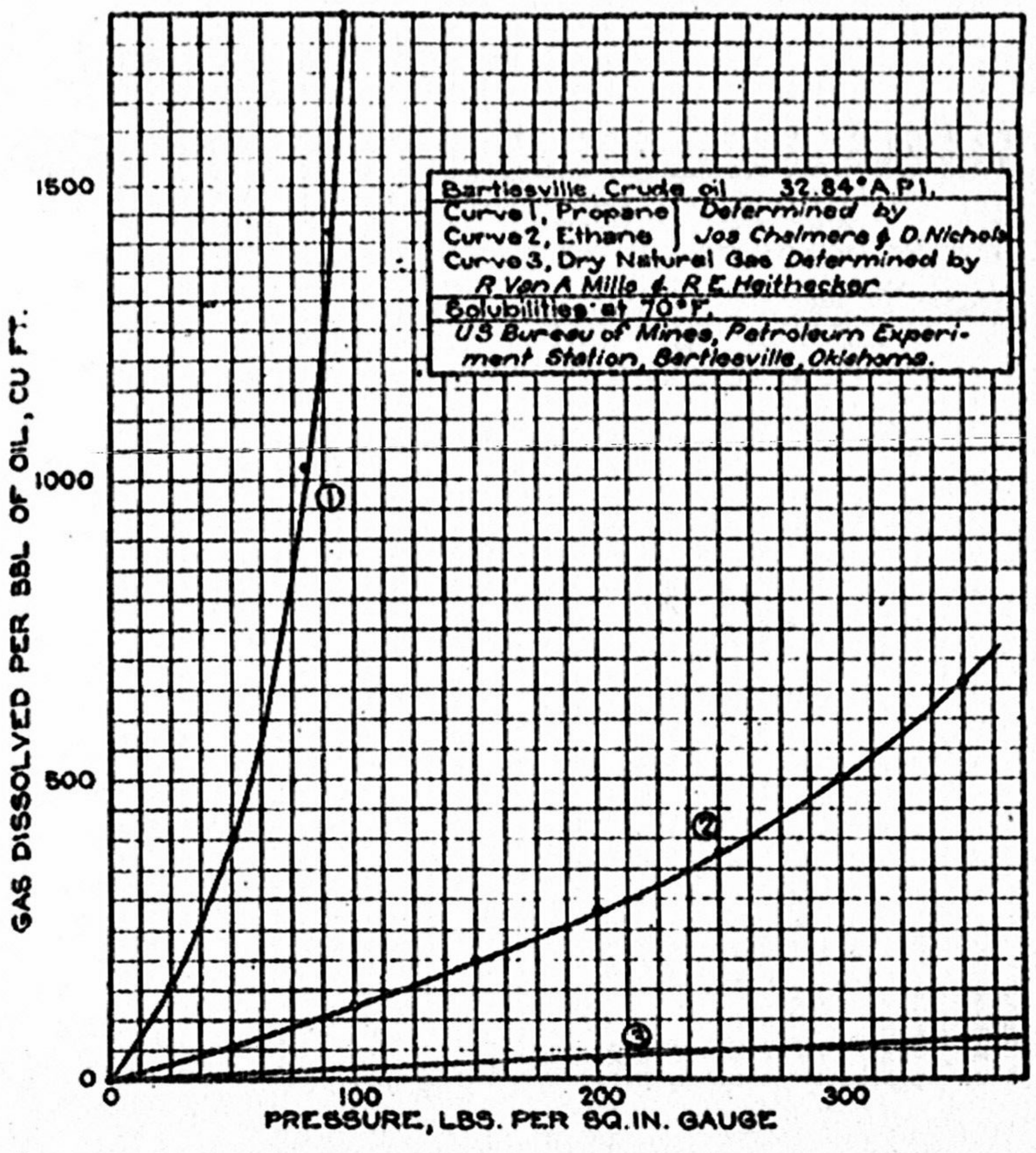

Figure 3—Variation of solubility with pressure, Bartlesville crude oil 32.84° A.P.I.

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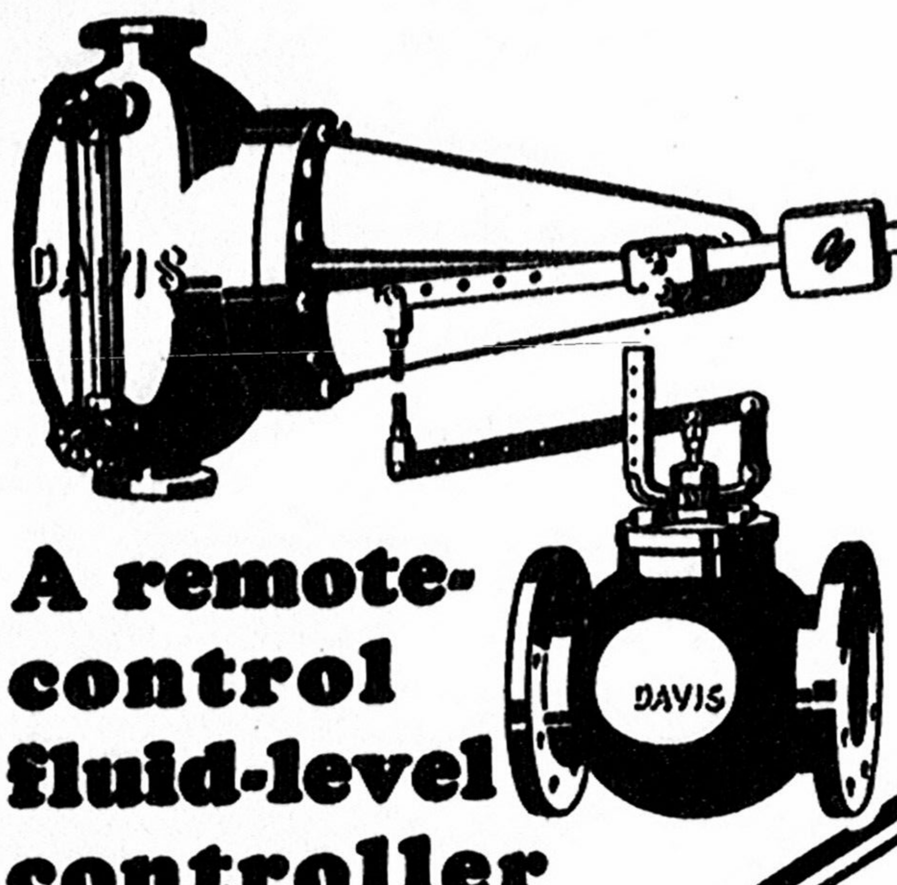

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(1) was closed, needle valve (6) opened slowly, and the gas under pressure in the separator assembly was drawn off and measured at atmospheric pressure in the manner applied to the upper range of pressures. In drawing off the final sample of gas in solution, the entire system was brought to atmospheric pressure with stopcock (1) and valve (6) open. The bomb was hammered violently.

Volume of Gas

The sum total of all of the gas given off at the different pressures was considered to be the total volume of gas originally in solution in the oil at the temperature and pressure under which the sample was taken at the well head. In arriving at amounts for calculation and for plotting curves to show pressure-solubility relationships, the actual total measured volume of gas was increased by an amount equal to the calibrated volume of the separator, the tubing connecting the separator with the measuring bottles and the shrinkage space above the oil in bomb (a) after the pressure was brought to atmospheric. The amount of gas in solution at any particular pressure, and water vapor was 5,665 c.c. In liberating this volume of gas, the oil reduced in volume approximately 1.5 per cent. The shrinkage space above the oil in the bomb was filled with gas at 1,396 pounds pressure, which when expanded to atmospheric pressure would have amounted to about 932 c.c., neglecting its deviation from Boyle's law. The overall effect of this deviation was within the limits of experimental error, therefore the total amount of gas liberated between the pressure 1,672 and 1,396 pounds per square inch absolute was the sum of the gas volume actually determined in the bottles, separator and assembly, and the gas confined in the shrinkage space at the top of the bomb.

Shrinkage Determination

The following is a brief explanation of the method used in determining shrinkage:

1. The total shrinkage resulting from liberating the dissolved gases from any sample was obtained by measuring in a graduated glass cylinder the quantity of oil left in bomb (a) after the sample had been reduced to atmospheric pressure. Knowing the total capacity of the bomb, and the volume of oil remaining in it, the percentage of shrinkage was readily determined.

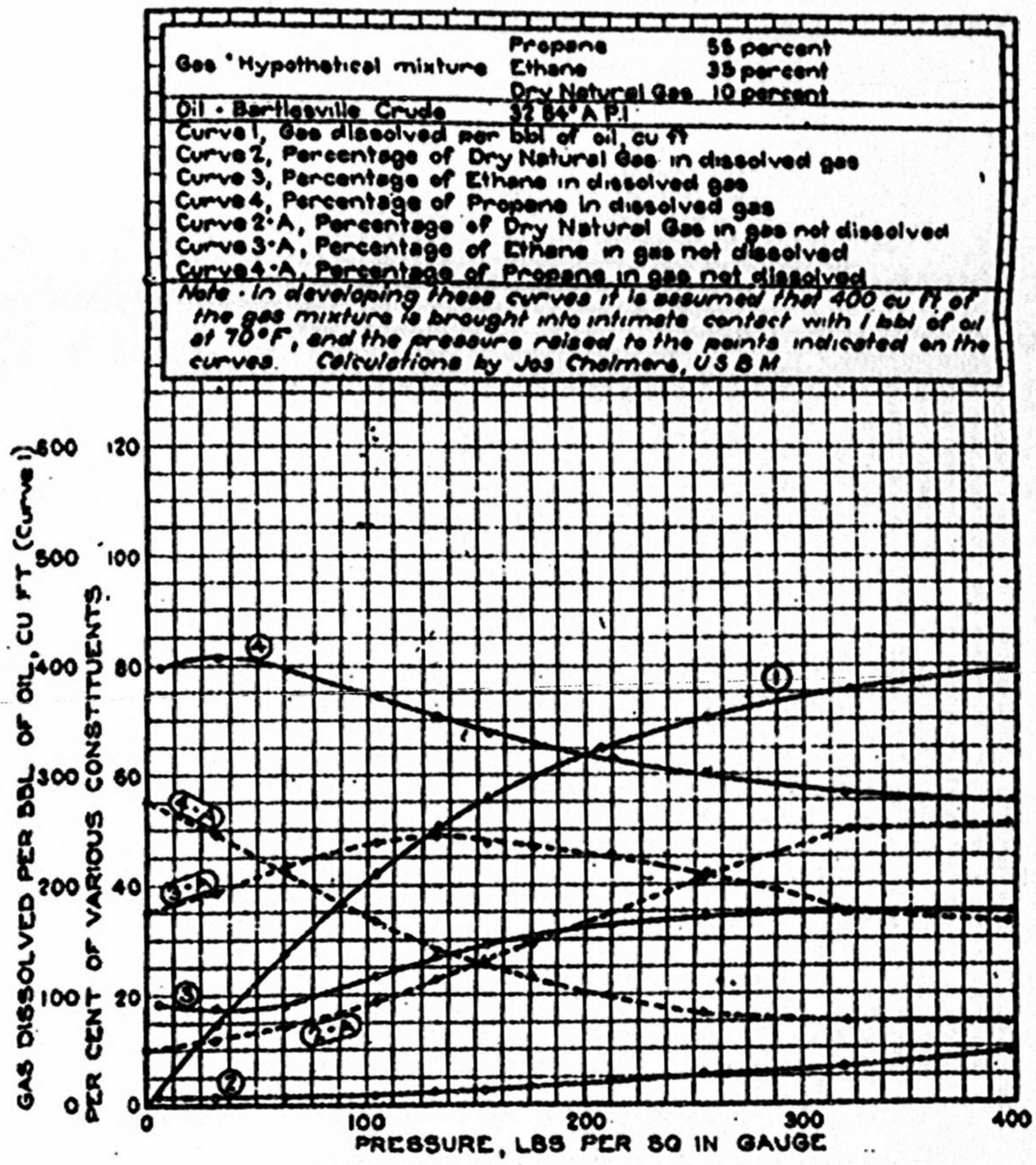

Figure 4—Theoretical solubility curves.

sure could readily be obtained by subtracting the quantity of gas given off above that pressure from the total amount of gas given off in reducing the sample from the original well head pressure to atmospheric. The gas-volume observations were reduced to a temperature base of 70° F. and a pressure of 14.4 pounds per square inch absolute. A further correction was made for the presence of water vapor in the gas because the gas was constantly in contact with water in the measuring bottles. The combined correction factor for temperature, barometric pressure, and water vapor ordinarily varied between 0.87 and 0.94. In developing the solubility curves (Figure 2), the reduction of volume of the oil due to the liberation of dissolved gas and the amount of gas under pressure occupying this shrinkage space above the oil was taken into consideration. At high pressures, especially, this made a considerable difference in the solubility curve. To explain: In reducing sample represented by curve 1, Figure 2, from 1,672 to 1,396 pounds per square inch absolute, the gas actually measured in the bottles and corrected for temperature,

2. The shrinkage at any intermediate pressure was determined by obtaining a sample at well-head pressure, and instead of allowing the sample to stabilize at well-head pressure, its pressure was gradually reduced by opening valve (3) at the top of bomb (b). If, for example, it was desired to determine the shrinkage at 400 pounds pressure per square inch, valve (3) was allowed to remain open until the pressure had reduced 50 or 60 pounds below the desired pressure. After closing valve (3), the pressure would be likely to build up to or above the desired pressure, and it would be necessary to vent more gas until the desired pressure was obtained. The sample would then be allowed to stabilize, and the procedure thereafter would be much the same as previously described. That is, the separator (Figure 1B) would be substituted for bomb (b), the gas would be drawn off into measuring bottles, and finally, when the sample was reduced to atmospheric pressure, the vol-

approximately 30, and for dry natural gas approximately 5.

For the purposes of discussion, assume a gas mixture containing 55 per cent propane, 35 per cent ethane and 10 per cent dry natural gas similar to the natural gas of which the solubility is represented by curve 3, Figure 3. These proportions are chosen by using as a guide the analysis of the gas liberated from solution in Kettleman Hills oil between pressures of 100 pounds per square inch absolute and atmospheric pressure. This analysis, as shown by the curves on Figure 5, is approximately 10 per cent methane, 35 per cent ethane and the remaining 55 per cent propane, butane and pentane.

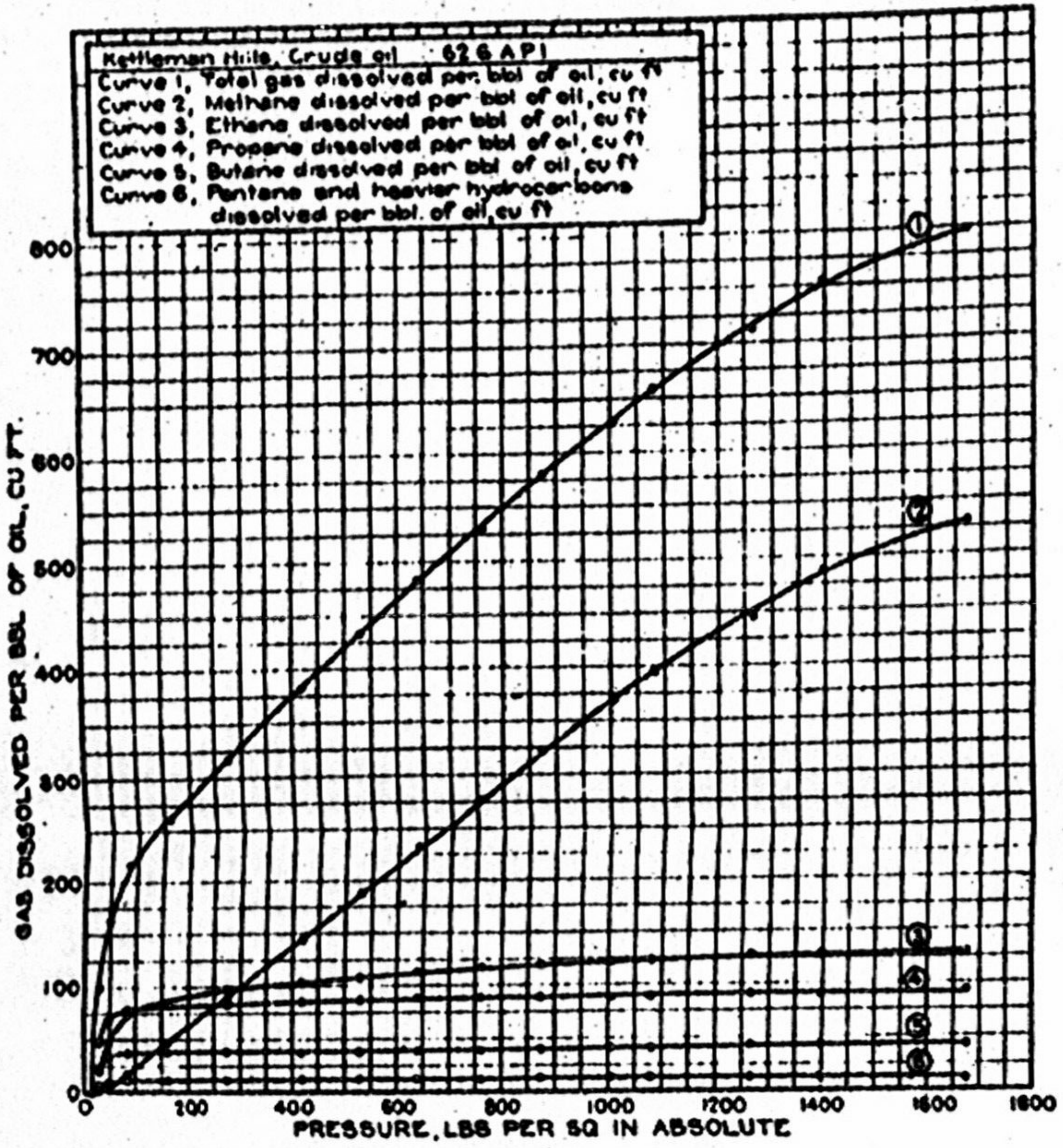

Figure 6—Solubility curves of gas in solution at 70° F. Kettleman Hills crude oil, 72.6° A.P.I.

Theoretical Result

The theoretical result of contacting 400 cubic feet of this hypothetical gas mixture with a barrel of crude oil has been calculated by Chalmers and is shown graphically in Figure 4. In these calculations, the solubility factors were determined from the curves shown in Figure 3, and the gases were assumed to dissolve in the oil in accordance with Henry's and Dalton's laws.

If 400 cubic feet of the specified gas mixture is contacted with a barrel of the crude oil used in the experiments recorded graphically in Figure 3 (32.84° A.P.I. gravity), and if the solubility factors indicated by Figure 3 are used, calculation based upon Henry's laws and Dalton's laws will show the results indicated in Figure 4. The curves in Figure 4 are not entirely dissimilar to those in Figures 2, 5 and 6. Compare the solubility curve (curve 1, Figure 4) with the corresponding curve (curve 1, Figure 5). Figure 5 is a graphical presentation of the results obtained from Kettleman Hills crude oil of 62.6° A.P.I. gravity. At 50 pounds per square inch gauge pressure, the theoretical curve (curve 1, Figure 4) shows a solubility of 113 cubic feet of gas per barrel of oil, whereas at 65 pounds per square inch absolute (50 pounds gauge) pressure, the Kettleman Hills oil shows a solubility of 193 cubic feet of gas per barrel of oil. Solubility of the hypothetical gas-mixture factors at gauge pressures of 100, 200 and 300 pounds per square inch is 205, 318 and 372 cubic feet of gas per barrel of oil, respectively, as indicated by the theoretical curve, whereas from curve 1, Figure 5, solubility at corresponding pressures is 235, 293 and 341 cubic feet respectively. It is believed that the theoretical and actual solubility curves as shown in Figures 4 and 5 respectively, conform closely enough to indicate that the solubility of gas in oil, plotted against the pressure, does not give a straight line throughout the entire range of pressures when the solubility is determined by measuring the gas released from an oil-gas mixture obtained under pressure from a natural reservoir.

In solving the foregoing hypothetical example, the results of which are shown graphically in Figure 4, attention is called to the fact that the conditions stated were definite and limited; that is, the quantity of gas was 400 cubic feet and the quantity of oil was 1 bbl. Similar conditions are found in nature; not necessarily in the same proportions, but certainly a definite amount of oil and a definite amount of gas exist in an undisturbed, natural oil reservoir. During geologic time these components reached a state of equilibrium. The gases that were capable of being absorbed under the definite conditions of temperature, pressure and ratio of the total quantity of gas to the total quantity of oil have long since been absorbed. The remainder of the gas, if there is an excess, remains associated with the oil but not dissolved in it.

It is important to consider these facts in defining and solving problems similar to that represented by Figure 4. A study of the curves in Figure 4 shows the selective solubility of the constituents of the hypothetical mixture at different pressures. For example, it will be seen that at 50 pounds per square inch pressure, 112 cubic feet of the hypothetical gas mixture was in solution (Curve 1). It is seen also that at 50 pounds pressure, 81 per cent of the gas in solution was propane (Curve 4). Therefore, 91 cubic feet of the total gas at 50 pounds pressure was propane. By similar procedure it was found that an additional 62 cubic feet of propane was in solution at 100 pounds; and of the remaining 67 cubic feet of propane, all but 8 cubic feet was in solution at 250 pounds pressure per square inch. The selective solubility of propane is well illustrated when these figures are compared with the amount of dry natural gas that was in solution at the same pressures. The figures for dry natural gas at these pressures are 1.5, 4.0 and 19.0 cubic feet per barrel of oil, respectively (Curve 3, Figure 3). Thus, at a pressure of 250 pounds per square inch gauge, 212 cubic feet of propane was in solution, whereas only 24.5 cubic feet of dry natural gas was dissolved.

Selective Solubility

This selective solubility naturally changed the composition of the gas not in solution. It will be remembered that the hypothetical gas mixture originally contained 10 per cent of dry natural gas, 35 per cent of ethane and 55 per cent of propane. Compare these figures with the analysis of the gas not in solution at 250 pounds pressure as indicated by curves 2-A, 3-A and 4-A of Figure 4. This indicated analysis is: Ethane, 42 per cent; dry natural gas, 41 per cent, and propane, 17 per cent. Of course these calculated analyses are not strictly correct, for the reason that no correction is made for the effect of the vapor pressure of the oil. This correction, particularly for weathered oil, would be so small that it has been disregarded in the present hypothetical case.

In the theoretical problem dealing with a hypothetical gas mixture, no account has been taken of the changes in volume, specific gravity and other properties of the oil that occur progressively as the oil absorbs the gas. If the composition of liquid is changing progressively, dependent upon the properties of the gases which it absorbs because of selective solubility under pressure (and liquefaction under certain conditions), and, in turn, the contacted gases are changing progressively in composition, it would not be expected that a straight-line relationship will exist between the solubility of the gas mixture in the liquid and the corresponding pressures.

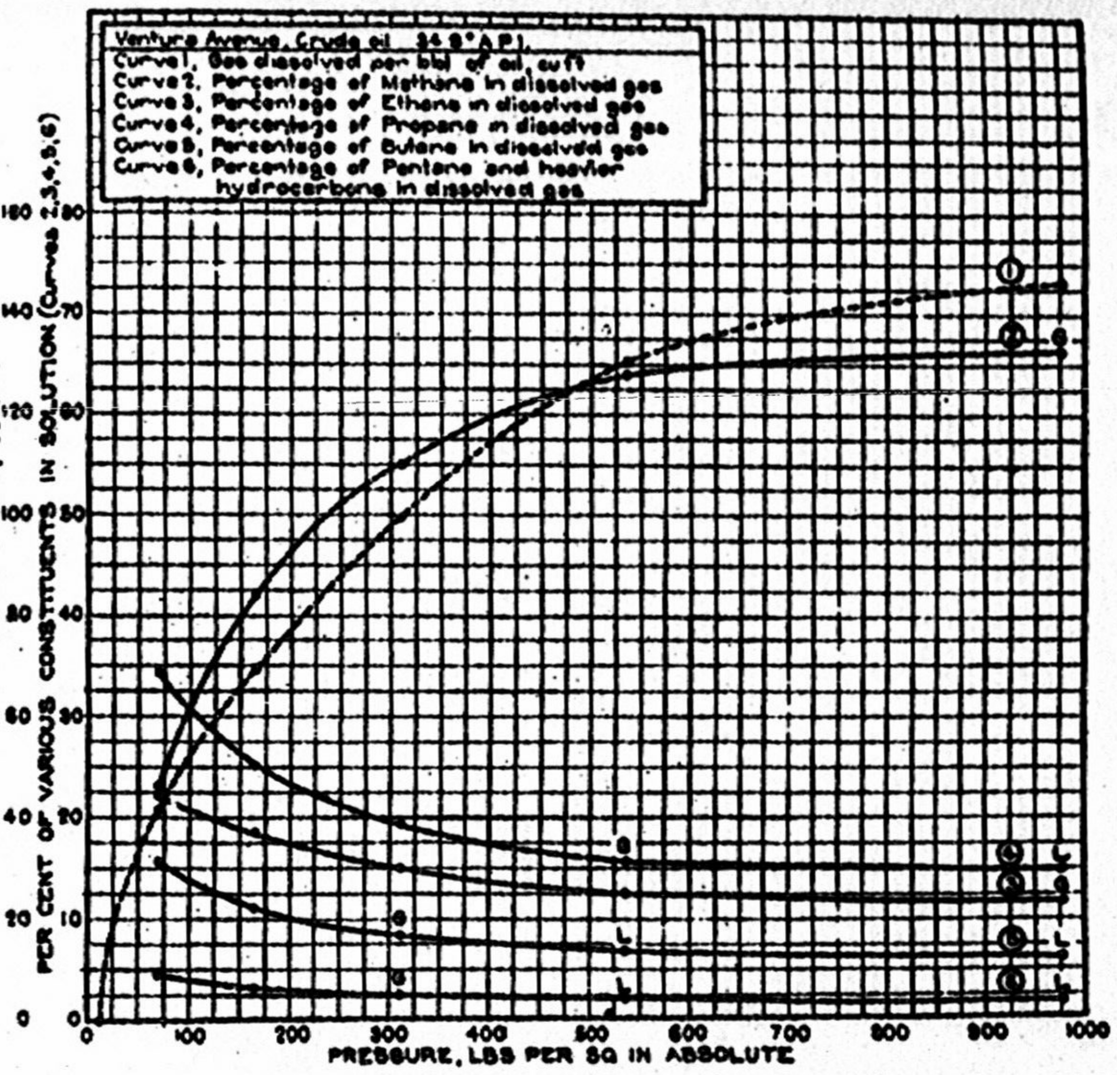

Figure 7—Solubility curves of gas in solution at 70° F. Ventura Avenue crude oil, 34.9° A.P.I.

In comparing the results of the present investigation with those of other investigators, it should be realized that they measured the solubility of a gas, containing some hydrocarbons relatively high in the series, in oil composed of hydrocarbons relatively low in the series. Under these conditions and under the further condition that no definite limit was placed on the quantities of oil and gas used, it might be expected that the solubility curves, within the range of pressures used, would be straight, or nearly so. In the present investigation, the entire range of hydrocarbons was represented in the gas and liquid. Some of the hydrocarbons that were gaseous under low pressure were in the liquid phase under high pressures.

In further explanation of the straight-line relationship, it may be well to consider the methods used where straight-line solubility curves were obtained. According to the published reports of these investigations, a new sample of weathered oil and a fresh sample of gas were used at each pressure point, and therefore the conditions of the tests reported by Beecher and Parkhurst and Dow and Calkin did not permit the progressive action of selective solubility. In other words, the gas that was put into solution at high pressures had the same constituents, in the same proportions, as the gas that was put into solution at low pressures. These conditions are not directly comparable with natural conditions in oil reservoirs, and therefore the oil-gas mixtures resulting from contacting oil and gas in the method described do not duplicate the oil-gas mixtures obtained under pressure directly from flowing wells.

Nature of the Gas in Solution

Curves 2, 3, 4, 5, and 6 (Figures 5 and 7) show percentages of the various components of the gas in solution at various pressures. The curves in Figure 5 indicate that the entire volume of gas dissolved at the maximum pressure contained 66.1 per cent methane, 16.1 per cent ethane, 11.3 per cent propane, 5.2 per cent butane and 1.3 per cent pentane and heavier hydrocarbons.

The action of selective solubility is clearly illustrated when the curves are read at lower pressure. For example, if the curves are read on the 100-pound ordinate, the following analysis of the dissolved gas is indicated: Methane, 9.8 per cent; ethane, 33.8 per cent; propane, 35.8 per cent; butane, 16.5 per cent; pentane and heavier hydrocarbons, 4.6 per cent.

The effect of selective solubility is shown by Curve 1, Figure 5. At an absolute pressure of 100 pounds per square inch, 230 cubic feet of gas were in solution per barrel of oil, whereas at the maximum pressure of 1,672 pounds per square inch absolute, the gas in solution is not 16.72 times the quantity in solution at 100 pounds but only 3.48 times this amount, or 800 cubic feet per barrel of oil.

Curves 2, 3, 4, 5 and 6 (Figures 5 and 7) were developed from the results of the fractional distillation analyses of the gas samples, liberated at the several observation pressures, to show the percentages of the constituents of gas in solution at those pressures. The total gas remaining in solution at any given pressure was considered to be 100 per cent,

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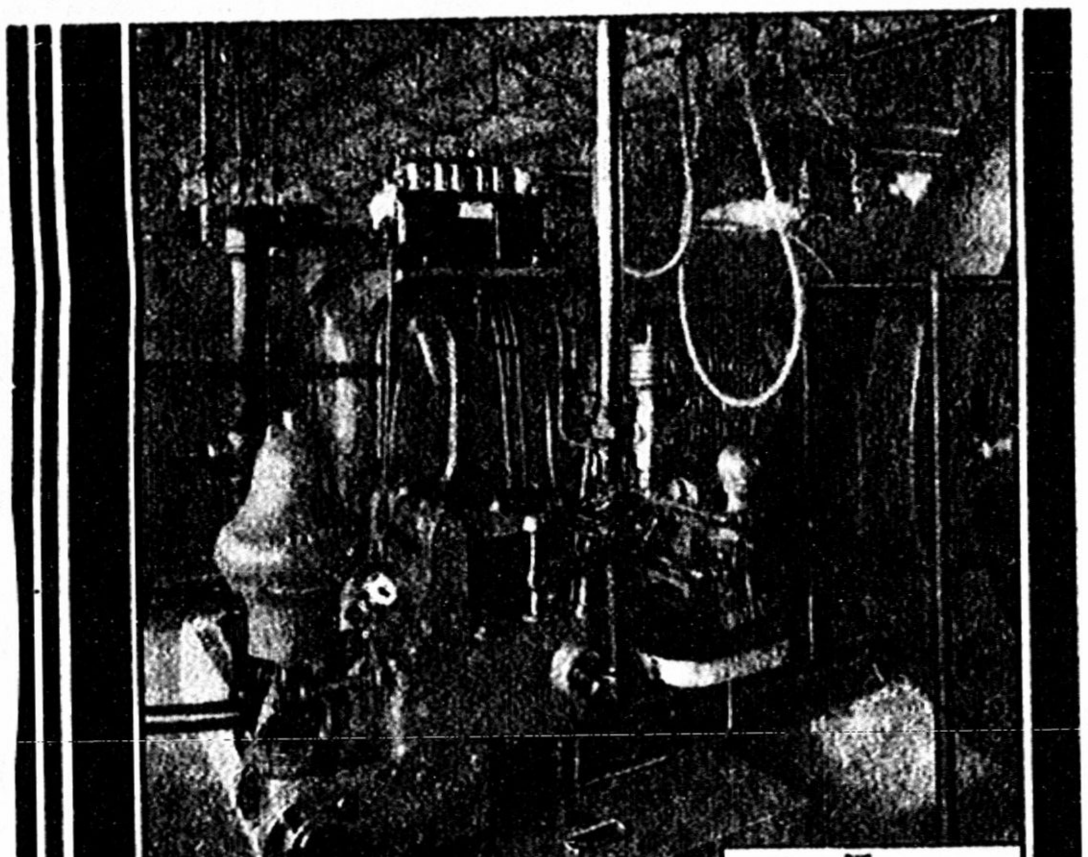

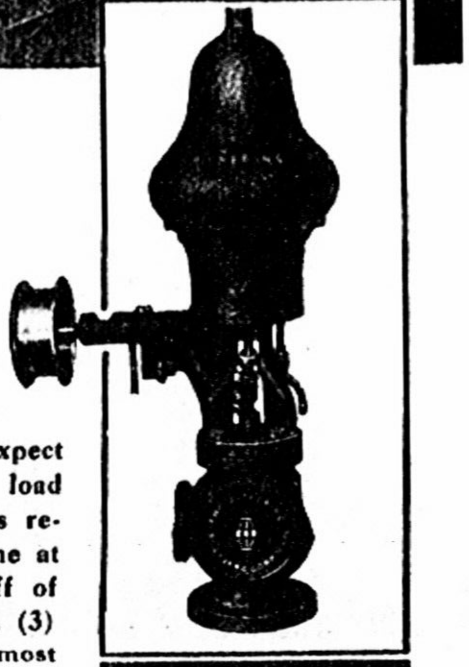

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even though the actual volume of all of the components of gas in solution at that pressure may have been only a certain percentage (for example, 25, 33, or any other actual per cent) of the total gas liberated throughout the entire pressure drop of the well-head sample from its initial pressure to atmospheric. The individual points for plotting the curve representing each component were obtained by arithmetical computations based upon the method of proportional parts.

The data shown in Figure 5 may be presented in another way. In Figure 6 the amounts of the various components of the gas in solution at any given pressure are plotted on the basis of cubic feet per barrel of oil instead of on the percentage basis used in plotting Figure 5.

Solubility Factors

The oil represented in Figure 5 has one of the highest solubility factors and the oil represented in Figure 7 has one of the lowest solubility factors of all of the oils tested. These charts have several interesting features. Attention is called to the peculiar reverse form taken by the ethane curve (3) at the 100-pound ordinate in Figure 5. Ethane is liberated in such large quantity at pressures below 100 pounds per square inch absolute that it might be thought to be changing from the liquid to the gaseous phase. This is not believed to be the case, however, as under the conditions of the test the partial pressure of ethane was below 573 pounds, and therefore the ethane must have been in the gaseous phase throughout the entire range of pressures. Hence, it is marked G (gas) at the maximum pressure. The heavier gases, however, are believed to have been in the liquid phase at the maximum pressure, as their respective partial pressures were sufficiently high to liquefy them at the existing temperature, 70° F. Propane remained a liquid until the pressure was reduced somewhat below 760 pounds per square inch absolute (Curve 4, Figure 5). The letter L indicates that it was in the liquid phase at that pressure and the letter G indicates the gaseous phase at 640 pounds per square inch absolute. Phase points G and L are also shown for butane and pentane, on Curves 5 and 6 (Figure 5), respectively. It was rather surprising to find that phase changes apparently have little effect upon the liberation of the various gas components. Possibly this is due to the fact that the various liquid hydrocarbons are infinitely soluble in each other—in other words, they are miscible in all proportions—and as the pressure on a hydrocarbon such as propane approaches the liquefaction pressure, the propane gas approaches "infinite solubility." Curve 1, Figure 3, seems to give credence to such an explanation. This curve tends to become vertical and therefore indicates infinite solubility as the pressure approaches 100 pounds per square inch gauge, although propane would remain in the gaseous state at 70° F. until a pressure of approximately 100 pounds per square inch gauge is reached. It is quite possible that the ethane curve (2, Figure 3) would show similar characteristics if its vapor pressure, approximately 573 pounds per square inch absolute at 70° F., were approached. A study of Curve 2, Figure 3, shows that at a pressure of approximately 250 pounds per square inch gauge this curve for ethane begins to deflect with an increasingly upward trend (its slope becomes greater with increased pressure), and if the pressure were increased to 550 pounds per square inch gauge, it is believed likely that the curve might become nearly vertical. From the data shown in Figure 3, however, there is no reason to believe that a methane curve would show an upward deflection, as the critical temperature of methane is —82.1° C. or —116.2° F., and therefore, regardless of pressure, it could not approach liquefaction at 70° F.

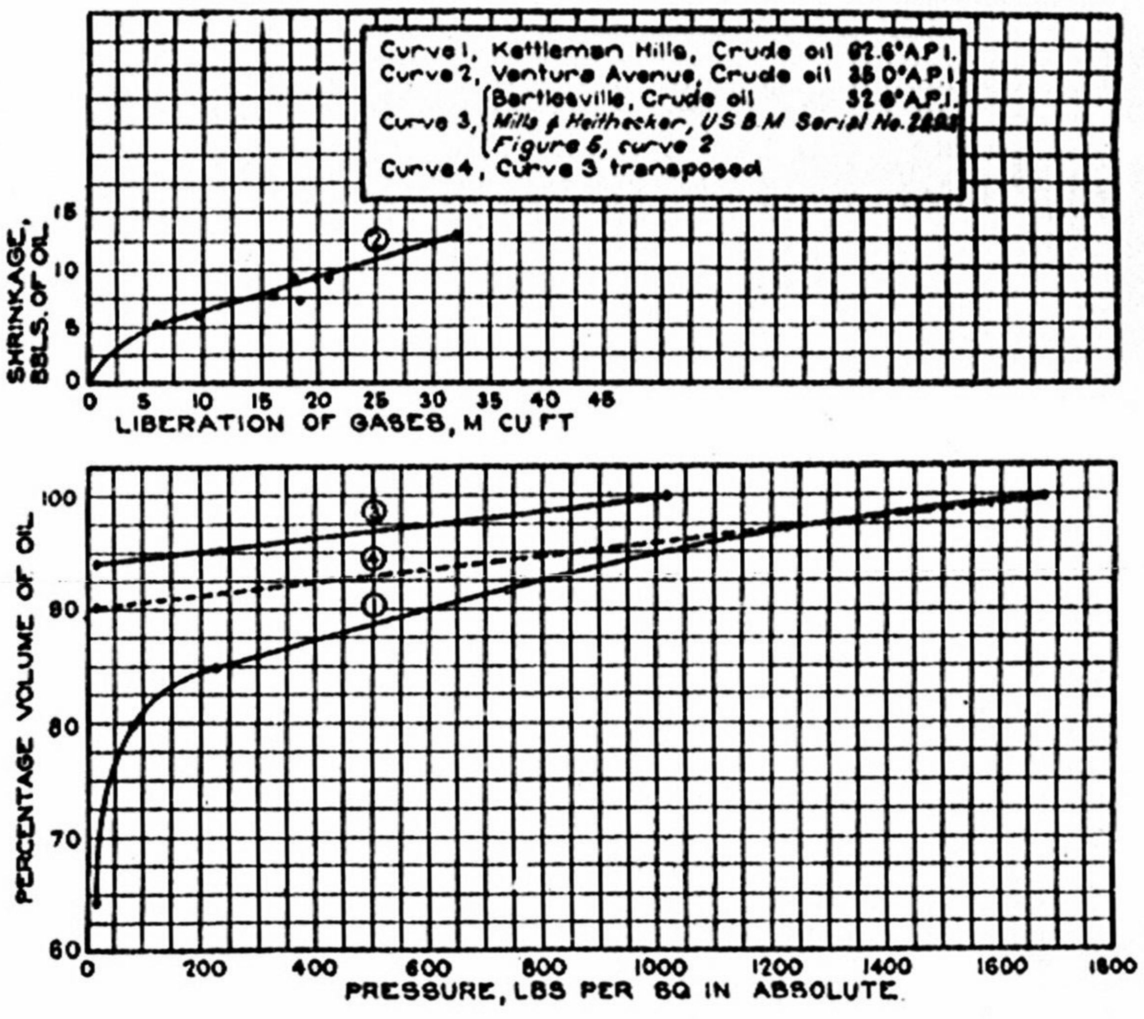


Figure 8—Shrinkage of oil due to liberation of dissolved gases.

One of the interesting features of Figure 7 is that propane is in solution in greater quantity than ethane in the Ventura Avenue oil. This oil is the only one tested so far that has shown this peculiarity. Also, no reverse appears in the ethane curve for this oil, as was the case for the Kettleman Hills crude shown in Figure 5. It is believed that such a reverse in the curve probably would have appeared if it had been practical to have taken gas samples at intermediate pressures between 68 pounds per square inch absolute and atmospheric pressure.

Shrinkage

Mills and Heithecker have reported the results of their experiments relating to the changes in volume of certain crude oils due to the solution of gas in those oils. In their experiments, the oils contained hydrocarbons relatively low in the series, and the gas dissolved in the oils contained hydrocarbons relatively high in the series. As the intermediate hydrocarbons, if present at all, were in relatively small amounts, it is not surprising that straight-line shrinkage curves were obtained as shown in Curve 3, Figure 8. Curve 4, Figure 8, is a straight line of the same slope as Curve 3; it was plotted from the 100 per cent point at 1,672 pounds per square inch absolute for Kettleman Hills crude of 62.6° A.P.I. gravity.

Curve 1, Figure 8, shows the volumetric changes at various pressures undergone by Kettleman Hills oil when its dissolved gas was liberated from 1,672 pounds pressure per square inch absolute to atmospheric pressure. Its volume at the maximum pressure is assumed to be 100 per cent. It is well to point out here that extreme accuracy is not vouched for in these shrinkage determinations, as the apparatus (Figure 1) was not designed for this purpose, and it was only through arduous and complicated procedure that H. C. Miller and the writer obtained the approximate data shown by Curves 1 and 2, Figure 8.

Curve 1, Figure 8, shows that a wellhead sample of Kettleman Hills crude oil of 62.6° A.P.I. gravity sustained a loss in original volume of approximately 36 per cent when the pressure was reduced from 1,672 pounds per square inch to atmospheric. During this reduction in pressure, at a constant temperature of 70° F., an equivalent of 800 cubic feet of gas per barrel of oil was liberated (Curve 1, Figure 5). Although true bottom-hole conditions of pressure and temperature in the well from which the sample was taken (or adjacent wells) are not known, it is not unreasonable to suppose that withdrawal of gas from solution in the reservoir will cause a reduction in volume of the liquid content of that reservoir which is comparable, and of the same order, with the results obtained in the present oil shrinkage study. If the above assumption is true, and knowing that 800 cubic feet of gas were liberated per barrel of 62.6° A.P.I. gravity in a pressure reduction of wellhead samples from 1,672 pounds per square inch to atmospheric, it could then be said that the total liquid content of the reservoir will have been reduced in volume approximately 0.36 bbl. for each 800 cubic feet of gas liberated from solution within the pressure range covered by the experimental work. This amount of shrinkage would be in addition to the depletion that can be measured in actual barrels of oil produced. The full significance of this shrinkage factor in computing normal decline and ultimate production of natural reservoirs which are under so-called volumetric control has not yet been determined.

It was necessary to plot Curve 2, Figure 8, of the Ventura Avenue crude on an entirely different basis from that used in plotting Curves 1 and 3, because of the wide variation in the solubility factors of this oil at virtually the same pressures. This variation in solubility probably was due to the fact that the well flowed by heads with a variation in pressure of more than 200 pounds per square inch during the process of taking an oil sample. The maximum pressure of 977 pounds per square inch absolute for the Ventura Avenue sample (Curve 1, Figure 7) is the pressure of stabilization after the bomb was disconnected from the well. Actually during the progress of taking this and other samples of Ventura Avenue oil, the well pressure at times went below and above the final pressure of stabilization. However, the pressure recorded was probably more constant than any other pressure observed during the sampling period.

Curve 2, Figure 8, shows that for each 32,000 cubic feet of dissolved gas that is liberated from this oil, within the range of pressures covered by the experimental work, there is indicated a possible shrinkage of at least 13 bbls. of liquid content of the reservoir, in addition to the depletion caused by the oil produced. Curve 2, Figure 8, also brings out a fact that is not shown directly in Curve 1, Figure 8. It shows that equal volumes of dissolved gas do not result in equal volumetric changes in the oil; for example, 5,000 cubic feet of the heavier gases occupy a space equal to 5 bbls., or roughly, an equivalent of 24 cubic feet per gallon. Comparison of the upper and lower ranges of this curve indicate that the oil shrinkage due to the liberation of the lighter gases is about one-third that of the heavier gases. This condition probably can be explained by the fact that the molecules of the heavier gases are composed of a greater number of atoms than the molecules of the lighter gases, also, they are actually larger in size and therefore occupy more space when in solution than do an equal number of molecules of the lighter gases. When out of solution, however, equal numbers of molecules of different gases occupy the same space when under the same temperature and pressure in accordance with Avogadro's law.

Gravity of the Oil

The gravity of the gas-saturated oil under pressure was not observed. However, it is not particularly difficult to arrive at an approximate value for this figure, by estimating the weight of the various gas constituents liberated. A gram molecule of any gas has a volume of approximately 22.4 liters at 0° C. and 760 mm. At 70° F. and 14.4 pounds pressure per square inch absolute, this volume would be 24.63 liters. Knowing the volume of the various components liberated, their combined weight in grams can be calculated. Also by knowing the volume of the bombs, which were filled originally with gas-saturated oil, and the volume and specific gravity of this oil when reduced to atmospheric pressure at 70° F., the weight of the original gas-saturated oil sample is the sum of the weights of the gas liberated and the oil recovered. Its specific gravity can be determined by dividing the weight of the gas-saturated oil in grams by its volume in cubic centimeters.

Such calculations have been made with reference to the oils represented in Figures 5 and 7, and results are shown in Table 1.

TABLE 1—ESTIMATE OF GRAVITY OF GAS-SATURATED CRUDE OIL

Kind of oil—	Gravity, °A.P.I. at atmos. pres.	Gravity of gas-saturated oil at well head pres., °A.P.I. (computed)	Well-head pressure of gas-saturated oil, lbs. per sq. in. abs.
Kettleman Hills	62.55	102.30	1,672
Ventura Avenue	34.87	38.94	977

It is interesting also to compare the gravity of the oils recovered after the dissolved gas had been liberated gradually to atmospheric pressure, with the gravity of these oils, as reported by the operators. Table 2 shows this comparison.

TABLE 2—EFFECT OF RATE OF LIBERATING DISSOLVED GASES UPON THE GRAVITY OF THE OIL

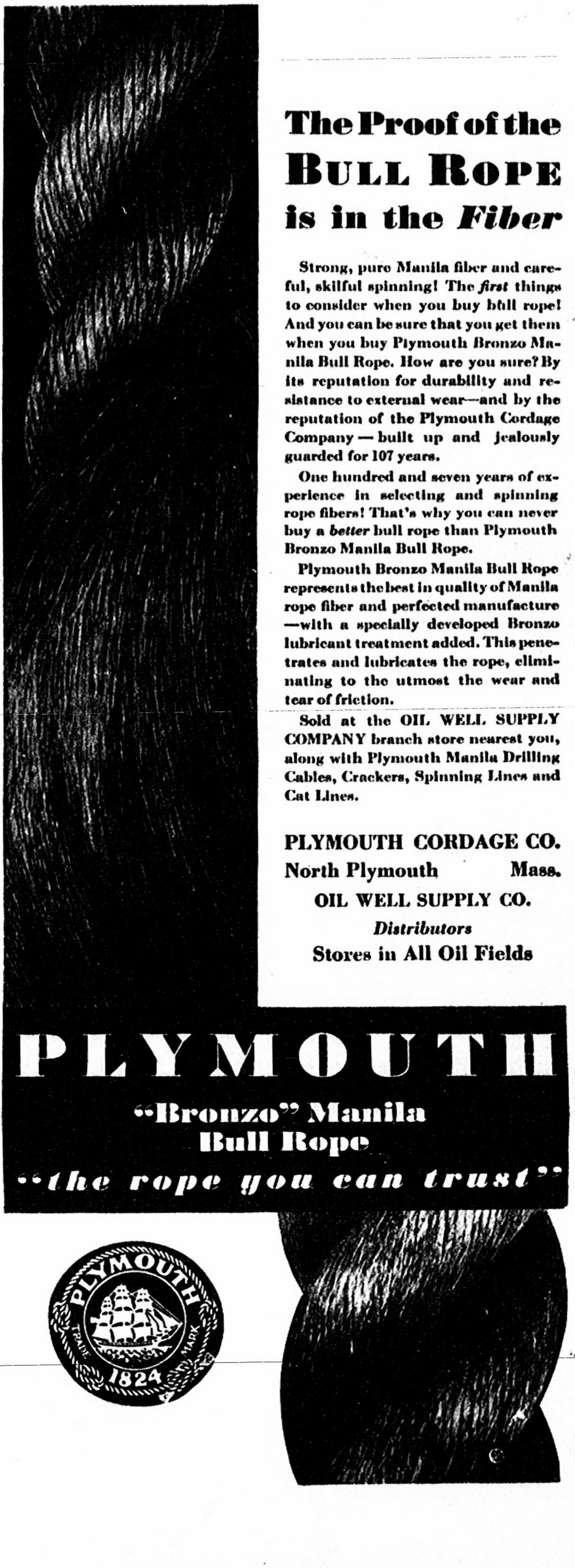
Field—	No. of samples	Average gravity of oil recovered in experiments, °A.P.I.	Gravity reported by operators °A.P.I.
Kettleman Hills	7	63.1	61.0
Kettleman Hills	5	44.8	40.0
Ventura Avenue	8	35.0	32.0
Oklahoma City.	2	43.0	39.9

The higher gravity resulting from gradual reduction of pressure is undoubtedly due to the retention by the oil of part of the propane fraction, large quantities of butane and pentane, and possibly some of the heavier hydrocarbons, which in field operations usually are carried away by a rapidly moving stream of gas when the pressure is released suddenly within the system. A system of trapping that would accomplish gradual separation at the highest possible pressures might be the means, under certain conditions, of not only increasing the value per barrel of the oil produced but also of increasing the quantity of oil by causing it to retain certain hydrocarbons which under ordinary trapping systems would become a part of the gas.

Nature of Gas Not in Solution at High Pressures

A sample of gas was taken from the delivery valve (3) of the upper bomb (b) (Figure 1) during one of the tests on the well at Kettleman Hills for which solubility curves are given in Figure 5. This sample of gas is believed to be representative of the free gas that was not dissolved in the oil at a pressure of 1,672 pounds per square inch absolute and 70° F. The following is its analysis: Methane, 85.6 per cent; ethane, 8.0 per cent; propane, 3.6 per cent; butane, 1.7 per cent; pentane and higher, 1.1 per cent.

By calculation, based upon field data not included in this present report, it



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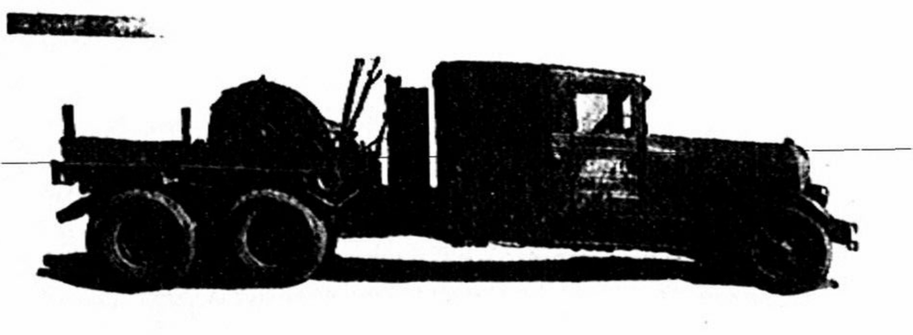

has been estimated that the quantity of gas not in solution at a pressure of 1,672 pounds per square inch absolute and 70° F. was equal to approximately 95.4 per cent of the total gas delivered by the well; also, other calculations indicate that this 95.4 per cent portion of the gas which was undissolved under the stated conditions contained approximately 91 per cent of total butane produced by the well.

Calculations have been made for the purpose of estimating the amount of natural gasoline contained in the gas not in solution at a pressure of 1,672 pounds per square inch absolute and 70° F. These calculations take into account the heavier fractions contained in the "pentane and higher fraction" and also take into account the fact that the final natural gasoline product which is produced in plant operation must not contain more than 31 per cent butane. The results of these calculations indicate that the gas not in solution at 1,672 pounds per square inch absolute and 70° F. contained approximately 0.411 gallon of pentane and heavier hydrocarbons per 1,000 cubic feet and 0.326 gallon of butane per 1,000 cubic feet; or, such gas contained a total of approximately 0.737 gallon of natural gasoline per 1,000 cubic feet.

General Statement

The results of this investigation show the solubility of gas in certain crude oils at various pressures from 1,686 pounds per square inch absolute to atmospheric, and at a temperature of 70° F. They do not show the solubility at the very high pressures which may exist underground and at temperatures of possibly 200° F. or more which have been indicated by geothermal studies. Whether the solubilities existing underground are greater or less than those shown in Figure 2 is not known. It is known, however, that increased pressure increases the solubility of gas in crude oil, and that within certain limits increased temperature decreases the solubility. It is known also that in distillation an increase in temperature results in the liberation of dissolved gases, and portions of the oil that are liquid at lower temperatures are vaporized at higher temperatures. In comparing the effect that experimental conditions had upon the results reported in this investigation with the effect that might be obtained if the experimental conditions approximated natural conditions more closely, the partly counteracting influences of increased pressure and of temperature must be considered. Higher pressures closely approximating those existing underground would cause more gas to be in solution in the oil (or to be in the liquid state) than the results obtained from well-head samples at flowing pressures have indicated. The effect of higher temperatures upon the solubility of natural gas in crude oil would be to decrease the amount in solution of the less soluble gases, methane for example, and to increase the liberation of the more soluble gases, propane and butane, that remain in solution in considerable quantity when a sample is reduced to atmospheric pressure at a temperature of 70° F. That these more soluble gases remain in solution in considerable quantity at atmospheric pressure and temperature is indicated in the introduction of this paper, where reference is made to the quantity of gas liberated by applying vacuum to Burbank crude oil. In addition to the increased liberation of the more soluble gases, certain hydrocarbons that would be in the liquid state at 70° F. would be vaporized at higher temperatures.

An estimate of the combined effect of these several and presumably counteracting factors upon solubility, shrinkage and amount of recoverable vapor when samples are reduced to atmospheric pressure under different temperature conditions is not attempted in this preliminary report.

DATA ON BOTTOM HOLE PRESSURES IN OIL WELLS

(Continued from Page 95)

only 15 pounds, showing that the tubing filled with fluid almost as fast as the gas pressure in the tubing could be released. The chart shown in Figure 5 was taken in a well producing at the rate of 2,200 bbls. of oil and 2,600,000 feet of gas per day through 8⅝-inch casing. The chart shows pressures at intervals of 250 feet in the flowing column of oil and gas. The excessive vibration of the gauge while at 3,925 feet was probably caused by the gauge hanging opposite a stratum of pay sand. The chart reproduced in Figure 6 was taken in a pumping well and is explained in a later paragraph. These charts are representative of a large number that have been obtained in wells producing under a wide variety of conditions.

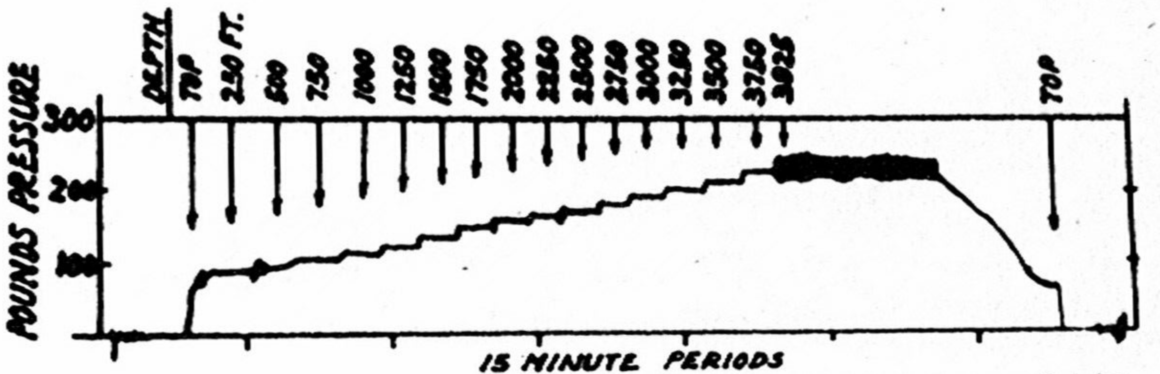

Figure 5—Pressure chart from well flowing naturally. The instrument was suspended for a time at each of the indicated depths.

Application of Bottom-Hole Pressures

The value of determining pressures in different formations while drilling through them is shown in the following table. These pressures were obtained in wells in the Carr City Pool in the Seminole district. Seminole County, Oklahoma:

Formation—	Top (feet)	Bottom (feet)	Pressure (lbs.)
Hunton	3,980	3,910	1,520
Simpson	4,068	4,124	1,152
First Wilcox	4,124	4,142	*637
Second Wilcox ..	4,217	....	†800

*Simpson and first Wilcox open to hole.
†Estimated from increase in fluid level.

Measured pressures in these formations permit certain precautions which might otherwise be overlooked. For example, in drilling it is the universal practice in the Seminole district to produce the small amount of oil which may occur in the Simpson with the "first Wilcox" sand. As these sands are usually drilled with cable tools, the much higher pressure in the Simpson would cause oil to flow from the hole into the "Wilcox" sand when the porous part of the "Wilcox"

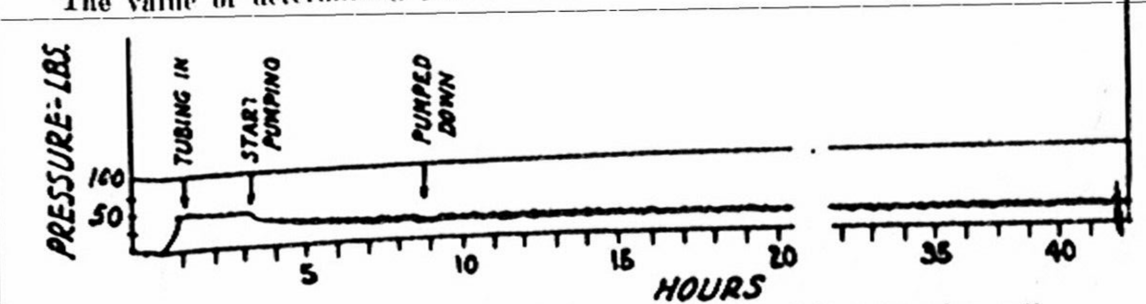

Figure 6—Record of pressure below working barrel in a pumping well.

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Solubilities of Gases in Liquids at High Pressure[1]

Per K. Frolich,[2] E. J. Tauch, J. J. Hogan, and A. A. Peer

Department of Chemical Engineering, Massachusetts Institute of Technology, Cambridge, Mass.

THE application of high pressures to industrial processes has led to engineering operations that frequently require a knowledge of solubilities of gases in liquids at pressures higher than those for which such data ordinarily are available. Examples of this type are the separation of gases by preferential solution in a suitable scrubber liquid and the condensation of vapors in the presence of non-condensable gases. Occasionally also the rate of a chemical reaction in the liquid phase is controlled by the solubility of a gaseous reactant.

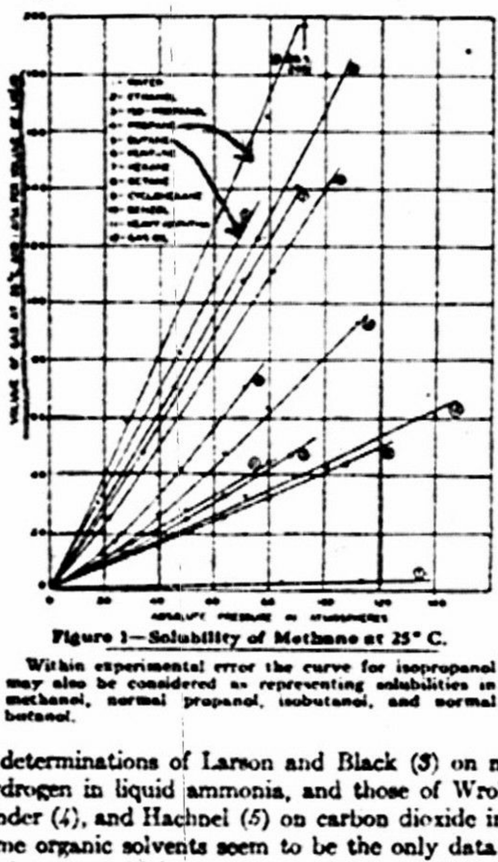

Figure 1—Solubility of Methane at 25° C.

Within experimental error the curve for isopropanol may also be considered as representing solubilities in methanol, normal propanol, isobutanol, and normal butanol.

The determinations of Larson and Black (3) on nitrogen and hydrogen in liquid ammonia, and those of Wroblewski (9), Sander (4), and Hachnel (5) on carbon dioxide in water and some organic solvents seem to be the only data on gas solubilities at real high pressures available in the literature. Finlayson (2), in attempting to develop a method of separating oxygen and nitrogen in air, studied the behavior of these gases toward various solvents at pressures not exceeding 160 pounds per square inch (10.9 atm.); and the solubilities of air and natural gas in kerosene, mineral seal oil, and various crudes have been determined by Dow and Calkin (1) at pressures up to 350 pounds per square inch (23.8 atm.). Larson and Black's data show that the amount of nitrogen and hydrogen dissolved in liquid ammonia is roughly proportional to the pressure up to 150 atmospheres. In the case of carbon dioxide, however, the linear relationship breaks down after the pressure has exceeded a few atmospheres, and thereafter the solubility is lower or higher than that calculated from the atmospheric data according to the solvent used (4).

Since these data did not permit of any generalization as to the behavior of other combinations of gases and liquids, a systematic study of the subject was undertaken. This work involved solubility determinations for a number of the common industrial gases in a variety of solvents, covering a wide range of pressure but limited to room temperature. Preliminary experiments by Simard and Sturznickle (7) on methane, nitrogen, and hydrogen in water and a series of alcohols gave results which showed in a qualitative way that the solubilities in such systems came close to being straight-line functions of pressure.

Experimental Procedure

Most of the solubilities were determined by saturating the liquid with gas at suitable intervals of pressure and measuring the ratio of solute to solvent in a sample drawn off for analysis. To this end a small amount of solvent was introduced into an evacuated steel cylinder of 2 liters capacity. The gas was then forced in at the highest pressure available and the cylinder agitated in a water bath maintained at 25° C. After the pressure had become constant, the cylinder was taken from the bath and inverted in a vertical position for withdrawal of a sample of the solution. The liquid and the gas separating from it on release of the pressure were collected over mercury in one of three burets, so designed that the volumes could be measured with the same degree of accuracy at any ratio of gas to liquid.

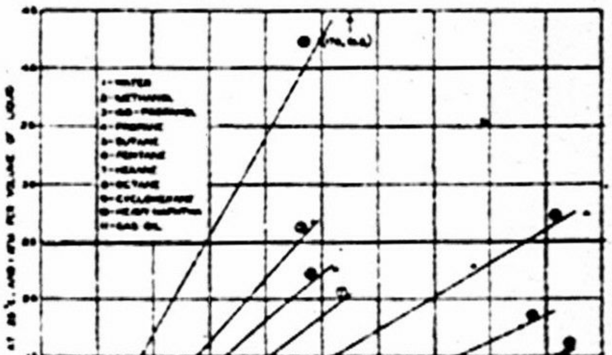

Figure 2—Solubility of Hydrogen at 25° C.

Within experimental error the curve for isopropanol may also be considered as representing the solubilities in ethanol, normal propanol, isobutanol, normal butanol, and benzene.

When the solvent was liquid at room temperature, as was usually the case, the two volumes were read directly and corrections made for the vapor pressure of the liquid and the atmospheric solubility of the gas. Since the liquid was atomized by the sudden release in pressure, complete separation of solute from solvent occurred without any sign of supersaturation, and it was only necessary to wait for drainage of the liquid before the volumes could be read. If the whole sample was in the gas phase, it was analyzed in an

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[1] Received March 6, 1931. Presented before the Division of Industrial and Engineering Chemistry at the 81st Meeting of the American Chemical Society, Indianapolis, Ind., March 30 to April 3, 1931.

[2] Present address, Standard Development Co., Elizabeth, N. J.

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at this mid-year meeting.* Our committee has approved Wescott's report, with the recommendation that the materials and methods described by him should not be used on too large a scale at first. They should be used gradually, and probably some machinery set up to observe the results obtained.

Regarding future work of the committee, a suggestion was received that certain work now under way in certain laboratories be carried on under the auspices of a joint committee from the committee on metallurgy and the committee on corrosion. This proposed work is an investigation of low-alloy steels for corrosion-resistance and corrosion-endurance properties. The matter was discussed with representatives of the corrosion committee, and it was suggested that any reports on this investigation, before presentation to the Institute, be subject to the approval of the corrosion committee which has a special sub-committee on materials. However, in discussing laboratory investigation on other metallurgical subjects, it was agreed that the committee on metallurgy contact such projects wherever possible, and, based on the merits of the results of the particular investigation, should sponsor their presentation and discussion before the Institute.

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* "Hard Surfaced Rotary Bits," Blaine B. Wescott (see preceding pages of this bulletin).

Topical Committee on Development and Production Research

DONALD E. DICKEY, *Chairman* †

A meeting of the Institute's production research committee was held in the Baker Hotel on Tuesday, June 2, at which time the proposed Institute program for research was discussed at some length in an effort to determine the best means by which the committee might aid in the continuation of research by the Institute and by individuals, public institutions or operating companies.

It was generally agreed that a function of the production research committee is to encourage and assist research by individuals, institutions or operating companies in an advisory, but not supervisory, capacity.

With this idea before the committee, the following plan was outlined for future work:

1. Each district will make a survey of the research work being carried on by operators or public institutions, and report such survey to a central agency.
2. This central agency (which for a time may of necessity be the national chairman and one or two other individuals) will attempt to analyze the data submitted, and return to all districts a summary of work under way or proposed. If it is found that several individuals are working on the same phase of a problem, an attempt will be made to suggest such changes as are necessary to broaden the scope of the research.
3. It is proposed to concentrate on those problems only which were chosen at the Chicago convention as most active and which were recently discussed by the advisory research committee on occurrence and recovery of petroleum.

It is planned to develop a definite procedure for obtaining progress reports from each district, so that the Institute may be kept informed on the activities of the committee.

W. N. Lacey presented a progress report on Institute Research Projects 36 and 37 dealing particularly with the study of rate of solution of gas in oil.

Definite and valuable progress has been made in this work, and continuation of these projects is already outlined for immediate action.

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† Broderick and Bascom Rope Co., Los Angeles, Calif.

EXPERIMENTS ON RATES OF SOLUTION OF OIL AND GAS

WILLIAM N. LACEY ‡

I probably may be kicking over the traces this evening in not preparing a set paper of any sort. It seems to me the sort of thing you might be more interested in would be an impromptu running report of what we have been doing on American Petroleum Institute projects at the California Institute of Technology at Pasadena.

This work started several years ago. I had the pleasure of being present at an interesting meeting at Ponca City just about the time we were starting this work, and there was a good deal of discussion on methods of production at that time. I was very much impressed with the facts which were known and the facts which were not known with regard to the process of repressuring. I came away from that meeting very firmly convinced that probably the subject on which there was the least information available was with regard to one particular phase of the repressuring process. We had some information as to the effects of dissolved gas on the properties of the oil which was suggestive and interesting.

Effect of Dissolved Gas on Properties of Oil

It seemed to me that, in the repressuring process, there are two factors we need to consider. The first is the maximum quantity of gas which can be put into a formation, related to the total solubility under given conditions; and, second, there is the time in which you can hope to get a given quantity in solution. I do not believe that there is any record available concerning the rate of solution of gas in oil.

We know, at least approximately, what the result may be in respect to changes in properties, but to get those effects we have to wait until the gas is dissolved; so I was convinced—and some of the American Petroleum Institute men agreed—that the work which was most needed then was some determinations of the rates of solution.

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‡ California Institute of Technology, Pasadena, Calif.

Later, it was requested that our Project 37 include, as well, work on solubility and the viscosity effects of dissolved gas. Project 35 (later changed to Project 36) was to determine the effect on surface tension. We have been working on these phases to a certain extent.

Work Started with Repressuring Point of View

I want to make it clear that the point of view with which we started this work was that of repressuring. In our work on rate of solution and our work on solubility, we worked from the angle of the dissolving of a given gas in a given oil material. That is a somewhat different direction from any that has been used before in solubility work. The attack, in the past, has been by causing the separation of a previously prepared solution.

Now, from the direct producer's point of view, I think that is possibly the angle to go at it. From the point of view of repressuring, however, it seems to us the other method of actually dissolving the gas in the oil is probably the better procedure. I have become more convinced of this as the work has gone on, in that I think we have a process which is capable of such reproducibility as to be somewhat superior to the other methods for that reason alone.

I wanted to point out, first of all, that there are two different methods of attack, and that we worked from the repressuring side. I have outlined the general topics upon which we have worked, and I want to go into the individual research problems more in detail.

I hope this will be very informal. Anyone who has a question, if I don't make myself clear, or a criticism he wishes to make may please speak up at any time. I would very greatly appreciate comments. One reason I was anxious to come and talk was to get new viewpoints on this work we are doing; so, if you have an interruption, please don't hesitate. Also, there is a good bit of talking that can be done; and if anyone gets tired and wants to leave, you won't bother me if you do.

Work on Rate of Solution

I want to speak first of the rate of solution work, which is the part of our Project 37 that we have carried more nearly to a satisfactory conclusion than the others. This has been under way since we started this project; several different men have worked on it. I want to make clear that this report covers the work of other men. It is sometimes the case that someone who does not do the work talks about it and the other people do not get full credit.

Four men have worked on this rate problem: N. F. Scudder and Frederick P. Stapp did much of the preliminary work. Mr. Scudder worked out a mathematical solution for the diffusion process, and Mr. Stapp carried out a large part of the preparation of samples, as well as making rate determinations. Earl S. Hill has made the more recent rate determinations. Richard D. Pomeroy has worked on the problem longest, and has contributed more than any other of the four men.

Now, the problem we set out to work on was that of determining the rate at which a given gas sample would dissolve in a body of petroleum oil. To have a simple situation for study, we can take a vertical cylindrical container which carries in it a certain body of liquid petroleum. We can close this up except for a gas inlet tube. Beginning with a pressure which is equal to atmospheric, we will suddenly raise the pressure of gas above this body of oil to a given higher value. The first thing that would happen would be solution of gas in the surface of liquid, and probably in a very short time the immediate surface would become saturated with gas at the pressure maintained above it. But the gas molecules going farther into the liquid would have to move from the surface by a process of diffusion due to molecular motion, travelling gradually down into the liquid. We felt sure that the original step of saturation of the surface film, requiring only a few molecules compared to those in the gas space above, would be a very rapid one, and that the time of solution would depend almost completely on the rate of this later process of diffusion.

We started out with a system very similar to this, consisting of a body of oil of known cross-section and a gas space above it which we could hold at a certain pressure. The quantities of gas which went into solution in this body of oil were measured over a period of time which would correspond to a fair percentage saturation of the whole body. The apparatus and method for doing this will be illustrated more in detail as we go along, but this describes the fundamental idea with which we started.

Amount of Gas That Enters System

Our first problem was to determine the gas which went into the system. This was measured by using a reservoir system, which was filled to a pressure two to three times the pressure which was to be maintained in the absorption system. It contained a pressure gage which we used as an indication of the quantity of gas contained in the reservoir system. For example, if we take an ordinary pressure gage and consider that as a reservoir system, filling it to 700 or 800 lb. pressure, we have in this system a certain quantity of gas. This quantity cannot be calculated easily, but by merely using the gage as an indicator and then calibrating the system we avoid these complications.

The system has been calibrated, not once but a number of times, by filling it up to a pressure of about 800 lb. and drawing off successive portions of gas into a mercury pipette at atmospheric pressure. In this way a calibration curve of quantity of gas withdrawn versus decrease in gage-reading is obtained. A more useful curve, derived from it, is that showing total quantity of gas in the reservoir versus gage-reading. We found the system to be a very reproducible one over long periods. By taking calibrations at intervals, any small trends in the system could be studied systematically and taken into account. After filling the gas reservoir and placing the correct quantity of oil in the absorption cell at atmospheric pressure, the system was made tight and gas was admitted from the reservoir to the cell to bring it to a definite pressure. The pressure was measured by means of a test gage which was calibrated against a dead-weight tester and checked at frequent intervals.

Now, what we did was to admit gas from the reservoir into the absorption cell. Of course, the minute you let gas in, there is going to be some solution; and it takes a short period of time to reach the desired pressure, readjust the temperature, Fig. 14 shows the absolute diffusion constant, the constant K in the equations shown in Fig. 4, plotted against the A. P. I. gravity of the liquids used. You can see that, for some reason—I won't guarantee to give you the reason—these points do fall in a rather orderly arrangement in correlation with A. P. I. gravity. I do not believe that is a real correlation. I do not see why density should be the controlling factor. It is much more likely some other factor, which we do not determine, is the true correlating property and very nearly parallels the A. P. I. gravity. The plot, at least, serves to give a summary of our results. If asked to make a "first guess" at the diffusion rate of methane in a given liquid, I would use this plot to determine it, but would not guarantee accuracy.

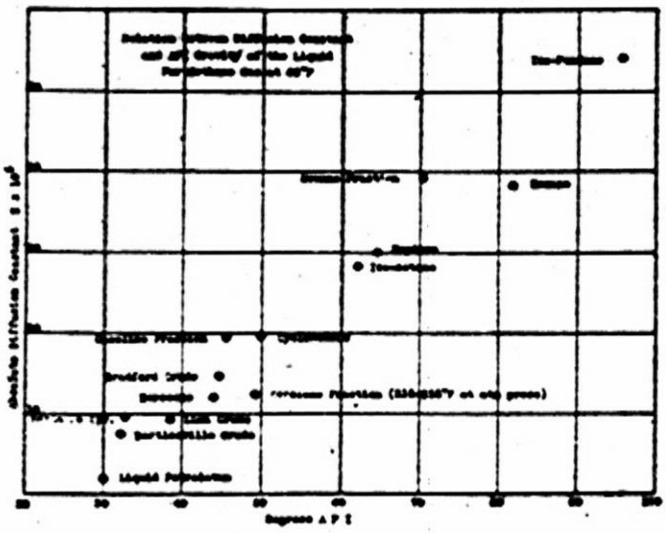

FIG. 14

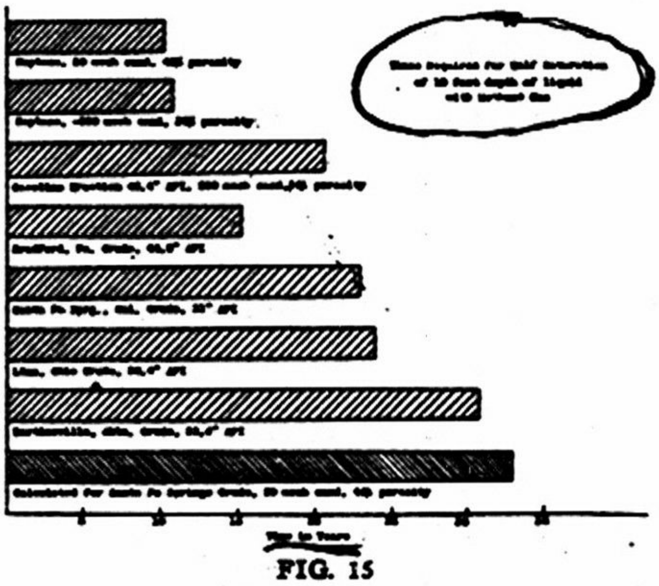

FIG. 15

Question: Have you tried to correlate rates with the molecular weights of the liquids?

Mr. Lacey: We have felt that the determination of average molecular weights of these somewhat impure liquids would be off our track, and so have no figures for such correlation. We have not felt, up to the present time, that we have enough data to indulge in statistical work.

There is one more figure (Fig. 15) which I thought might bring this data back to a more practical basis for visualization. We have taken the case of heptane in a 20-mesh sand of 45 per cent porosity, and have calculated the time required to half saturate a 10 ft. depth of liquid with methane gas above it: that is, we have assumed a 10 ft. depth of liquid which contained no dissolved gas, and brought gas above it at an increased pressure and let it diffuse into the liquid until it was 50 per cent saturated. It must be remembered in this connection that the first half of the gas dissolves much more rapidly than the latter half. This calculation tells us that at the end of about nine years this 10 ft. depth of heptane in 20-mesh sand would be approximately 50 per cent saturated. The other cases shown tell a similar story. The last case only is not based on experimental results. We have made no determinations thus far involving crudes in sands. To calculate the results for this last graph we have assumed that the diffusion constant for this crude in a sand would be reduced by the same proportion of its value without sand as was found to be the case for heptane with and without the same sand. It probably gives us the order of magnitude, at least.

Other Phases of the Work

There are several other phases of our work which I will try to run through very rapidly.

The solubility work which has been carried on has also been carried on from the viewpoint of repressuring. We have about 14 crude oil samples from various parts of the country. We have been working on the study of solubility of certain natural gases in these crudes. Our problem is to determine the amounts of these gases which can be dissolved in these crudes under a variety of conditions of temperature and pressure. We, therefore, carry the process on by dissolving rather than by separation from solutions previously prepared.

Bruce H. Sage has been responsible for the development of our method.

Our process is a relatively simple one. In this case our work is carried to pressures approximately 2,500 lb. per sq. in. instead of lower pressures, and it became necessary to take our gas samples and actually compress them to the pressures we wanted.

Our gas samples come in through a measuring reservoir system of exactly the same principle as was used in the rate work, except that we must have a greater volume in the system than that of our gage. The gas is withdrawn from the reservoir system, the amount let out being determined from our gage reading. It passes into a mercury displacement pump, shown in Fig. 16. It consists of a steel U-tube in which we have mercury. The gas sample of known volume is then compressed and pushed over into a saturation cell. This has a known volume of liquid in it, and the cell is agitated to bring about saturation. We are now concerned with equilibrium, and not with rates. The pressure is measured by a test gage which we have accurately calibrated and checked at regular intervals. We have two cylinders of high-pressure air from our liquid air machine to furnish motive

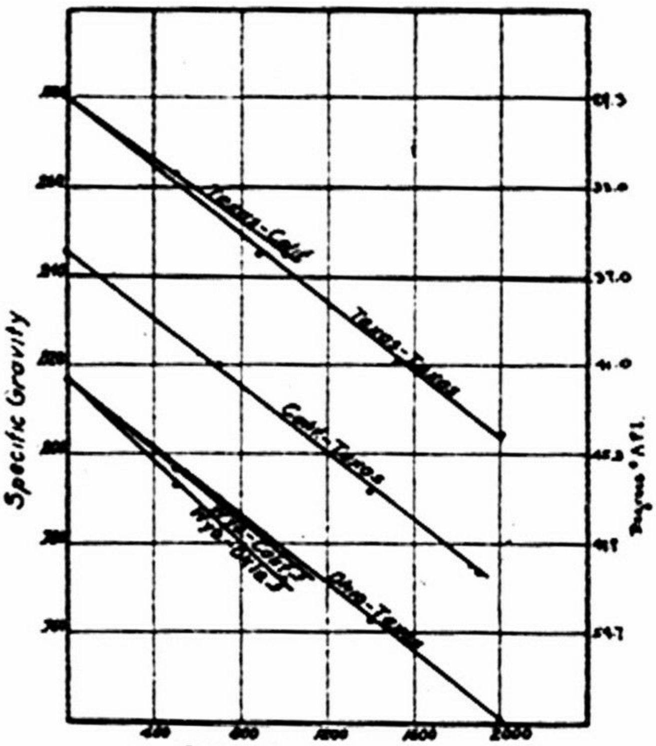

FIG. 22

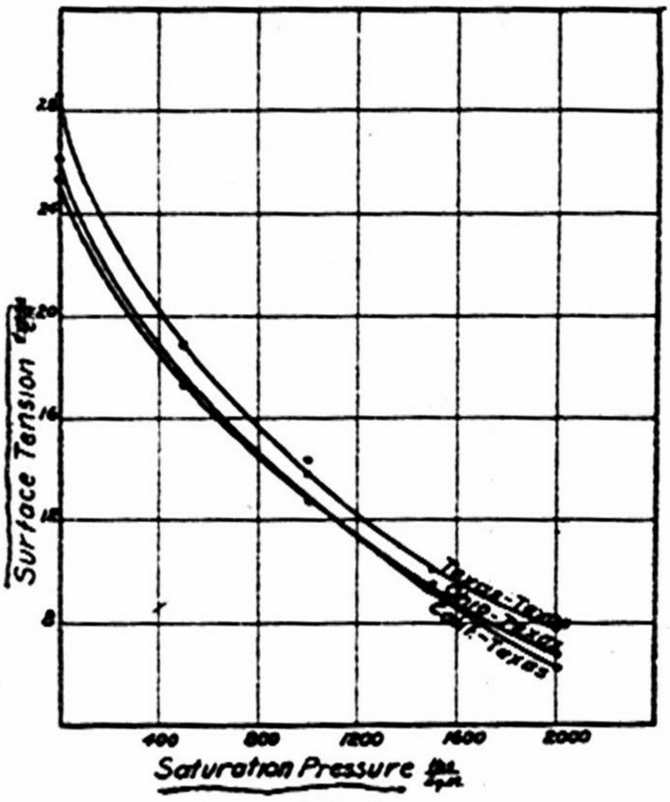

FIG. 23

oils. There is a very large range in surface tension, and at the highest pressure it is still changing rapidly. It would be interesting to see how these curves would look extended to 3,000 lb. pressure.

Fig. 24 covers various combinations of gases and oils. If given the original surface tension of an oil and a curve for a given gas you get, as far as these curves indicate, a pretty good approximation of what the surface tension might be for another oil and the same gas, if the original surface tension of the new oil be known. This can be done, because the curves for a given gas appear to be nearly parallel even if the original surface-tension values are rather different. Different gases give curves of widely different slopes.

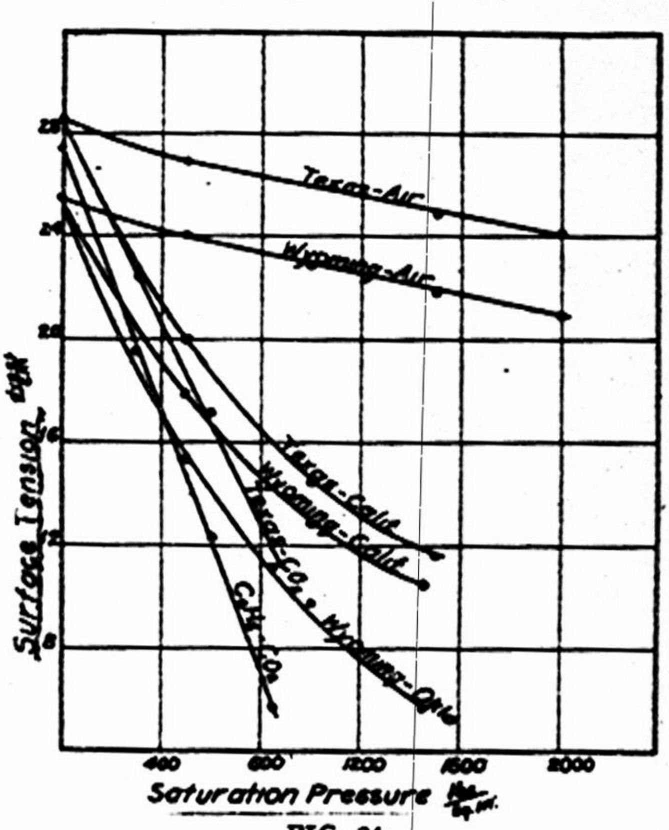

FIG. 24

Mr. Dickey: Has anyone any questions or comments they wish to make on these determinations that Mr. Lacey has discussed? I think that Mr. Lacey's discussion on these papers has not only confirmed some of our present views, but has advanced our knowledge considerably in Institute Project No. 37. It looks as if the advisory committee of the Institute had picked the right problem to keep on their list.

Mr. Lacey: Our work on viscosity has been preliminary. We have tried out several types of apparatus. The problem is a rather difficult one, because large ranges of viscosity are to be met with, and to get an apparatus which will give you accurate results in a wide range of viscosity over wide ranges of temperature and of pressure is no easy task. After some preliminary work which confirmed our belief in the apparatus, we have decided on a rolling ball type of viscosimeter. It consists of a tube, very carefully polished and of uniform

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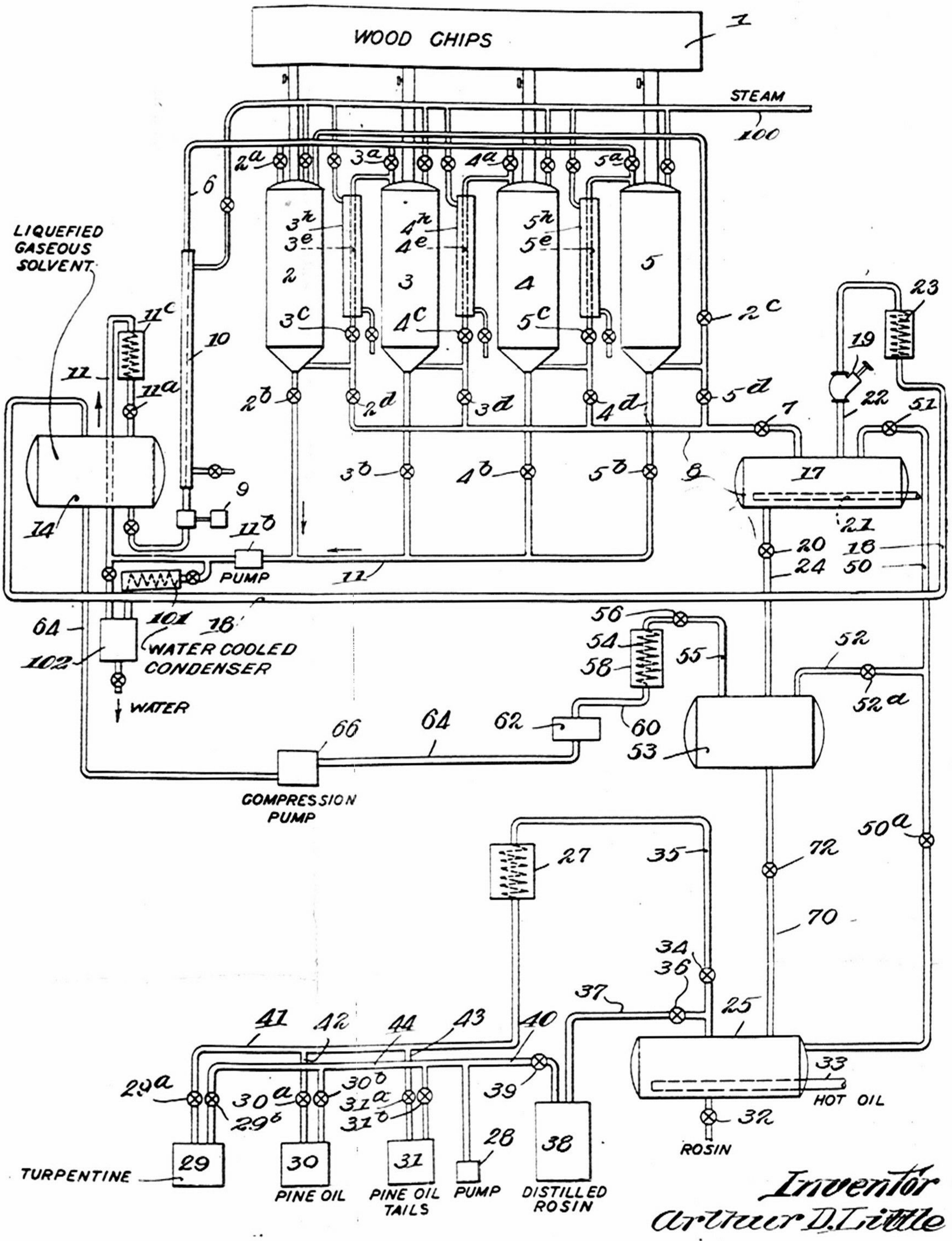
June 10, 1930. A. D. LITTLE **1,762,785**

PROCESS FOR THE SOLVENT EXTRACTION OF WOODS

Filed Oct. 8, 1927



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Patented June 10, 1930 **1,762,785**

UNITED STATES PATENT OFFICE

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PROCESS FOR THE SOLVENT EXTRACTION OF WOODS

Application filed October 8, 1927. Serial No. 224,865.

My invention relates to a process for the solvent extraction of solutes from difficult or protective inclusions, and typically useful for removing from coniferous woods hydrocarbon-soluble extractives, preferably selectively.

Broadly speaking I find that the dissolving properties of a solvent and its diffusion into the pores of a cellular material containing the solute vary inversely in respect to the molecular weight of the solvent. I have found that a solvent of such low molecular weight and low boiling point as under normal conditions of temperature and pressure to be gaseous, is when liquefied an ideal solvent, for the above reasons.

My invention includes in one aspect a treatment exemplified by the solvent extraction of a solute from the narrow cellular or intra-cellular spaces of solute-containing materials by treatment with the liquid state of a normally gaseous solvent; for further example, by a process for the treatment of coniferous woods for recovery therefrom of the contained extractives by the use of a hydrocarbon solvent substantially consisting of hydrocarbon materials which under normal conditions of pressure and temperature are gaseous and which due to its physical properties of fluidity and lack of resistance to penetration of minute voids, which qualities are an accompaniment if not a consequence of a low average molecular weight, possesses the property of rapid diffusion into and through the small ducts of the wood in which the resins and terpenes are contained. A typical process according to this invention is particularly designed for the extraction of rosin and the terpenes from the stump wood of the long-leaf yellow pine. I have found that if a solvent of low specific gravity and low average molecular weight is employed it more efficiently dissolves the rosin, turpentine and pine oil out of the coniferious woods without substantially dissolving any of the darker rosin-discoloring impurities in the wood such as are now removed by solvents in use.

Heretofore all commercially practical processes for the recovery of rosins and terpenes from coniferous woods by means of solvents have required that the wood be quite finely reduced as by shredding with the result that the residual wood after extraction has not been well adapted to the manufacture of paper pulp and is of little value except as fuel. One purpose of the present process is to make unnecessary such fine mechanical reduction of the wood prior to extraction, and to make it possible to efficiently extract chips of a size that are well adapted to standard pulp mill operations. This is accomplished by the use of a solvent of the physical properties associated with a relatively low average molecular weight to insure a rapid diffusion rate into and through the chips.

A further advantage of my invention is to provide a suitable chip of coniferous wood for use in paper making from which the rosin has been substantially extracted without any substantial degeneration of the cellulose therein, as occurs when the wood is steamed. By employing my invention I am enabled to substantially extract the rosin from chips of standard paper making size which chips produce a higher grade paper than the small chips or shreds.

One advantage of this process from the point of view of conserving useful fiber for paper making lies in the avoidance of any temperature causing the loss of tensile strength of cellulosic fibers in after treatment for paper making, such as the sulphite process particularly, and the avoidance of contributing degenerating treatment with superheated steam. In respect to the sulphite process relative completeness of extraction of resins is important to successful use of the paper pulp for making paper.

Another advantage of this process is its availability for treatment of relatively moist materials without damaging or expensively thorough pre-drying. Normally gaseous solvents of the type herein described contain components, notably butane, capable of solution in considerable amounts in water; either this capacity or the possible solubility of water in the liquid phase of the normally gaseous solvent may contribute to the observed capacity rapidly and effectively to dissolve resins in the presence of capillary inclusions of water in amounts which would inhibit treatment with ordinary solvents. For example, moisture contents of from 15% to 20% by weight have little or no effect on the operation of the herein described solvent on the rosin solute.

Another object is the simultaneous extraction of resins and terpenes without the necessity of first pre-heating to remove the latter, as by distillation with superheated steam or otherwise, which partially breaks down the resins into bodies that are undesirable in the ultimate resin product, and at the same time lowers the value of the residual wood for pulping by degeneration of the cellulose. The simultaneous extraction of the resins and terpenes is made feasible by the use of a solvent that boils substantially below that of the terpenes contained in the wood, but forms therewith no constant boiling mixture with any of the constituent terpenes, thus making it possible to readily separate and recover the solvent from the extractives for reuse.

A further object of my invention is the recovery of a lighter colored resin than has so far been obtained by the solvent extraction of woods rich in resins, such as the stumps of the long-leaf yellow pine. An example in support of this statement is the fact that wood rosin, as the trade knows the product of solvent extraction of long-leaf yellow pine, is generally of an F grade, as referred to the color standards of the United States Department of Agriculture, according to which rosin is graded progressively by letter designation from B to X as the color lightens from a dark reddish amber to a light amber. By the process of this invention it is possible to produce much lighter grades of wood rosin than heretofore obtainable, rosin of N and even higher grade being readily attained.

Yet another object is to recover rosin that is adapted to the present uses of so-called gum rosin, which is obtained by bleeding the living tree. For example, in one of the largest uses for rosin, which is in the manufacture of soaps, wood rosin as now obtained is entirely unsuited, for the reason that soaps made therefrom are either initially dark in color, or tend to darken on exposure to air during a comparatively short time. Rosin made by the process of this invention is entirely suited to manufacture of a high grade rosin soap. This product is also superior to present-day wood rosin in other important uses, such as in the manufacture of varnish and paper size, wherein gum rosin is today used almost exclusively.

The desirability of accomplishing the foregoing objectives which are now realizable has long been recognized, and much effort has been expended, in particular, to improve the grade of wood rosin. For this purpose various solvents have been suggested from time to time, but gasoline, or a middle fraction thereof, has remained in general use. I have discovered that the desired results can be obtained by the use of a solvent comprising a hydrocarbon of comparatively low molecular weight, preferably comprising one or more of the lower members of the paraffin or olefine series of hydrocarbons. These exert a marked selective action on the rosins, failing to extract a substantial proportion of the bodies which are responsible for the dark color in wood rosin and leaving these bodies in a condition not detrimental to use of the wood for paper pulp. I have found that hydrocarbon solvents having an absolute vapor pressure at 75° C. (a preferred working temperature), in excess of one thousand mm. of mercury, and less than twenty thousand mm., are ideally suited for the purpose of my invention. Hydrocarbon substances coming within this range have a relatively low average molecular weight, and their use at the preferred working temperature involves extraction under pressure to keep said substances liquefied. I have found that propane, butane and pentane alone or in admixture comply with the above specification and are ideally suitable, though as stated other materials may be employed and I have also actually used amylene and butylene. A suitable mixture will in general be found to have an average molecular weight lying between 28 and 77. I have further determined that a portion of even the higher paraffin series can be tolerated, but that with increasing average molecular weight, the rate of extraction falls off, and the recovered rosin is of lower grade.

My preferred solvent, in part because of availability at a price lower than motor fuel, is a mixture comprising chiefly butane. Fractions from petroleum or natural gas containing large proportions of such a material may today be regarded as a waste product from the operation of casing-head gasoline plants, wherein they are the product of the fractional distillation of the originally "wild" casing-head gasoline. When casing-head gas is scrubbed with oil or otherwise processed for the recovery of condensibles, there is extracted from the gas a portion of the contained propane and butane, which for purposes of transportation and use for blending with heavy naphtha to make a motor fuel is generally "stabilized," by which step is meant the separation of the normally gaseous propane and of substantially all of the butane. From this operation there may be first separated by treatment satisfactory for stabilizing the remainder a mixture of butanes and propane containing also some pentanes, which mixture without further treatment is satisfactory for use as an extractive solvent; but there is advantage in preparing from the butane-propane-pentane mixture for the present use a preferred material comprising a so-called butane fraction which can be prepared from the butane-propane mixture by fractional distillation, preferably under pressure. For example, a material so prepared of the following composition is entirely suited to the present purposes:

Propane, 9%; butane, 89%; pentanes, 2%.
Weathering: Initial boiling point, 15° F.
Test: Final boiling point, 32° F.; Sp. gravity, 0.573.

The present process thus provides a new solvent for resins, described herein in relation to its use with respect to the extraction of resinous woods, but the utility of this new solvent is wider than this described use and the advantages involved in its use will be apparent to those skilled in the art of extracting sundry materials with hydrocarbon solvents. For example, such a light hydrocarbon solvent can be employed with advantage to the extraction of vegetable oils, such as cocoa butter and corn oil, the degreasing of wool, the cleansing of fabrics, in rubber manufacturing, etc. This invention, in so far as it involves this solvent, is therefore not limited to extraction of any particular material from any specific environment.

So far as I am aware the only use for butane at present is as fuel. Since butane is normally found in gaseous form in gasoline plants, it is usually burned in the distillation plant in gaseous state as a fuel. So far as I am aware I am the first to provide a material containing available liquefied butane or to discover its special utility as a solvent or to observe the specially desirable solvent properties of such materials as applied to the treatment of coniferous woods.

A further object of my invention is to provide a novel process for the continuous extraction of materials in solvents, which comprises continuously extracting said material in an extraction unit, preferably a continuous multiple counter-current (serially operative) extraction unit, continuously separating the solvent and solute from the material, continuously distilling the solvent from the solute, continuously condensing the solvent and returning it to the extraction unit in a closed system, while maintaining a sufficient pressure in the system to keep the solvent liquid in the extraction unit, and preferably in addition, substantially stripping the last traces of the solvent from the solute by flash vaporizing the solute bottoms, condensing the recovered solvent and returning it to the extraction unit. While this feature of my invention may be employed for the extraction of various types of materials with various solvents, it is peculiarly useful for extracting rosin from coniferous woods. I have found in practice that with a distillation unit alone for distilling the solvent from the solute, it is substantially impossible to remove the last traces of solvent from the rosin and the terpenes without raising the temperature of the distillation tank so high as to disintegrate or discolor the rosin and terpenes. By flash vaporizing the bottoms from the distillation tank into a larger unit under the same heat, it is apparent that the pressure in said larger unit may be lowered sufficiently to permit the last trace of solvent to volatilize therefrom without any rise in temperature and that if desired the temperature in the distillation unit can thus be kept below the discoloring or disintegrating level.

Further objects of my invention are to provide various novel products produced at different stages in my improved process. First a novel resin-containing extraction product, secondly, a novel resinous product produced when the solvent has been distilled therefrom which may be readily transported if desired in liquid form in tank line or tank car for the further purification treatment; purer initial turpentine and initial pine oil than has been produced hitherto without refining; and lighter grade wood rosins than have heretofore been produced by any process involving the use of a hydrocarbon solvent.

The application of my invention to the extraction of rosin, turpentine and pine oil from such resinous woods as the long-leaf yellow pine will now be described with reference to the accompanying flow chart:

I preferably employ a battery of pressure extraction tanks, 2, 3, 4 and 5, connected together to operate successively and preferably continuously in counter-current fashion on the coniferous wood being treated. Chipped or shredded wood is fed from hopper 1 to the first three of the battery of extractors, 2, 3, 4 and 5, which may be of any desired size or construction. Before introducing the solvent it is desirable to eliminate air from the system, and therefore the air is preferably evacuated. This step also reduces explosion danger to the minimum and avoids the introduction of air into the closed butane system. Valve 2^a in line 6 leading from the butane storage tank 14 is then opened to admit the solvent to the extractor 2. Unless definitely stated that a valve is opened, it is assumed to be closed. The valves 3^c and 4^c leading into the next adjacent tanks are opened, tank 5 being temporarily withdrawn from use for cleaning and refilling purposes. Valves 4^d and 7 in line 8 leading to the butane distillation tank 17 are then opened. The material thus is cir-

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from the original bound volume

culated through line 6 by means of the pump 9 through the valve 2^a into extraction tank 2, out of filling line 3^e through the open valve 3^c into the extraction tank 3, out of filling line 4^e through the valve 4^c to the extraction tank 4, and out of extraction tank 4, through line 8 and through the valves 4^d and 7, to the distillation tank 17. If desired, as is shown, the solvent inlet pipe 6 may be provided with a heat interchanger 10 to preheat the solvent before entering into the extraction tanks. After the solvent has been circulated through the extraction tanks 2, 3 and 4 for a period of time sufficient to thoroughly extract the rosin and terpenes therefrom (in the unit described the time for extraction was four hours) the extraction tank 5 now refilled with chips and exhausted of its contained air is cut into the system by closing valve 2^a and the valve 3^c in the line 3^e. The valve 4^d is also closed. The solvent is now circulated through the line 6 through the valve 3^a to the extraction tank 3, from tank 3 through the filling line 4^e through valve 4^c into the tank 4; from extraction tank 4 through valve 5^c in the line 5^e to the extraction tank 5 and out of tank 5 through the valve 5^d in the line 8 through the valve 7 to the distillation unit 17. While a battery of only four extractors is shown, it is apparent that more may be employed in use if desired.

After the cycle of operations is first started, in order to successively employ the counter-current principle a new tank is cut in at the desired point in the extraction cycle. When any number n of tanks are employed and the extraction period occupies t hours, a new tank may be cut into the system every $\frac{t}{n-1}$ hours. It is obvious, however, that at the starting point tanks 2 and 3 are subjected to less extraction than they will be subsequently subjected to when the whole system has been operating for t hours or more. It is thus apparent that counter-current extraction methods are employed as fresh solvent is pumped on to the wood which has been previously subjected to solvent more or less saturated with extractive, the freshly charged wood always being first extracted with a solvent more or less saturated with the extractives, and the partially extracted wood being treated with fresh solvent. If desired, 3^e, 4^e, 5^e may as shown be provided with heaters 3^h, 4^h, 5^h, etc., in order to compensate for radiation losses from the extraction tanks and maintain a desired temperature in the several extraction tanks.

Before removing the wood from the respective extraction tanks, caution should be taken to remove all the hydrocarbon by pumping out any remaining solvent, then applying a vacuum to draw any remaining traces of solvent through the valves 2^b, 3^b, 4^b and 5^b respectively in the lines leading to the return line 11 to the tank 14 through the open valve 11^a therein by means of the pump 11^b in said line 11 followed preferably by a steam distillation under diminished pressure. For example, steam may be let into the respective extraction tanks through any suitable steam connection at 100. The solvent vapor as discharged in this manner can be recovered by compression or condensed at atmospheric pressure by means of an ammonia-cooled condenser 11^c and returned as a liquid to the storage tank 14. Preferably water taken up from the wood, if any, or condensed from the steam distillation, is condensed in the water cooled condenser 101, and separated at 102 from the hydrocarbon solvent whenever necessary.

I also provide a unit suitable for the continuous distillation of the solvent carrying the extractive, which separates the solvent by evaporation or distillation from the extractive, the solvents being distilled, condensed and returned as a liquid to the storage tank 14.

This unit comprises an evaporator and still 17 operated under pressure in a closed pressure circuit and continuously heated by the steam coils 21 and the vapors therefrom passing through the pipe 22 (valve 19 being opened), being condensed in condenser 23 and continuously returned through line 18 to the solvent storage tank 14. The evaporator or still is so designed that as much of the solvent as possible is removed from the extracted materials without a damaging rise of temperature. To maintain the solvent liquid in the still 17 and extraction tanks, I preferably insert the back pressure valve 19 in the exit line 22 forming a part of the closed pressure circuit.

Whereas the distillation of solvent in still 17 is conducted under pressure, it may be found inadvisable to recover all of the solvent at this stage owing to the necessity of either employing too high a temperature in the still 17 or resorting to a prolonged distillation period, either condition being apt to injure the rosin. It is therefore recommended that the distillation of solvent in still 17 be discontinued when the rate of distillation begins to fall off and that the contents of still 17 thereafter be discharged through line 24 to flash still 53 wherein the pressure is dropped, for example, to substantially atmospheric pressure. This latter operation will be found effective to release the remaining traces of solvent in the rosin-turpentine-pine oil mixture. The solvent vapors from still 53 are condensed in 54, 58, which may be ammonia cooled, and the resulting liquid collected in tank 62, from which it may be periodically discharged by compression pump 66 into the main solvent storage tank 14.

The mixture of rosin, turpentine and pine oil substantially stripped in still 17, and stripped of the last traces of solvent in still 53 is discharged through line 70 into the rosin still 25, wherein the turpentine and pine oil are separated from the rosin by means of distillation into several cuts, preferably turpentine, pine oil and pine oil tails in the tanks 29, 30 and 31, respectively.

A stated, I preferably provide a flash stripping still 53 and condenser unit 54, 58 having means 52, 55, 64, 66 to maintain a circulation therethrough to remove the last traces of the solvent from the extractives from the still 17, and operated under a lower pressure than the primary solvent still, the circulation means being connectable to the primary solvent still 17, and to the receiving tank 14.

When it is desired to remove the extractive through the line 24 to the still 53, the pump 9 will be completely stopped and valve 7 in the line 8 closed. Valve 19 in the line 22 is also closed and the valve 20 in the line 24 is opened. Vent lines 50 and 52 are provided to equalize the pressure between stills 53 and 17 to allow a free flow of the extractive to the stripping still 53, and when the extractive is being withdrawn from still 17 to still 53 valves 51 in said vent line 50 and valve 52^a in the line 52 leading from the line 50 to the still 53 are opened. At all other times these valves are closed. This allows the extractive to run from the still 17 through the valve 20 in the line 24 to the still 53. When sufficient extractive has been drawn to still 53 valve 20 is closed and valves 7 and 19 are opened and then the circulation of solvent is continued as before.

As the heated solute containing a portion of the solvent is drawn down the pipe 24 into the vaporizing still 53 the pump 66 is regulated to maintain a lesser pressure in the stripping still condensing unit than in the distillation still 17. It is apparent that with the drop in pressure all traces of the remaining solvent will be released out of the extractives in the vaporizing still 53, and led through the pipe 55, the valve 56 being opened, into the condenser 54 where they are condensed and pumped by the pump 66 through the line 64 into the receiving tank 14. It is thus apparent that by the introduction of this flash stripping still condensing unit into the closed system that it is possible to strip the last traces of solvent out of the extractives without raising the temperature high enough to degenerate or discolor the terpenes or rosins.

When it is desired to remove the solvent-free extractives through the line 70 to the rosin still 25, the pump 66 is completely stopped, the valve 20 in the line 24 closed, the valve 56 in the line 55 closed and the valve 72 in the line 70 opened, and the valves 50^a and 52^a in the vent lines 50 and 52 opened, which valves are closed at all other times. This allows the substantially solvent free extractives to run from the vaporizer 53 through the valve 72 in the line 70 to the still 25. When sufficient extractive has been drawn to the still 25 valve 72 is closed.

It is recommended that vacuum be used according to the observed results and the degree of heat of the heating medium for still 25 supplied in heater coil 33 while distilling at least the pine oil fractions, and usually the turpentine fraction, in order to avoid overheating the rosin in still 25. For this purpose I provide a vacuum pump 28 connected to turpentine receiver 29, pine oil receiver 30 and pine oil tails receiver 31. When the last of the pine oil tails has been separated from the rosin, valve 32 may be opened for the discharge of the hot rosin, unless it is to be vacuum distilled, into receiver 38.

Thus in practice I raise the temperature in the rosin still 25 by means such as the hot oil coils 33 until substantially all of the turpentine is distilled therefrom through the open valve 34 in line 35, condensed in condenser 27, and led into the turpentine tank 29, with or without opening valve 29^b to line 44 and vacuum pump 28, if desired with no vacuum up to an end point of 150° C., valve 29^a then being opened the valves 30^a and 31^a being closed. After the turpentine has been taken off into the tank 29, the line 41 leading thereto is closed at valve 29^a, valve 29^b is closed and the valve 30^a in the line 42 leading to the pine oil tank 30 is opened. In order not to affect a decomposition of the pine oil and rosin by raising the temperature of distillation, the vacuum in the pine oil tank 30 may now be increased by operation of the vacuum pump 28 at a higher rate and by opening the valve 30^b in the line 40 leading thereto. When the pine oil has been substantially removed, while still maintaining the vacuum I then open the valve 31^a in the line 43 leading to the pine oil tails receiver 31, close the valve 30^a in line 42 and open the valve 31^b in the line 44 leading thence to the vacuum pump 28, after closing the valve 30^b, and then raise the temperature up to substantially 200° C. to remove the pine oil tails into their tank 31. This substantially strips the rosin in vacuo of all bodies which would tend to cause discoloring on exposure and more effectively removes and cleanly cuts the pine oil tails than has been possible in any method of rosin extraction of which I am aware.

The turpentine and pine oil recovered in the above manner may require a subsequent refining and redistillation to meet market specifications. Usual operations for this purpose form no part of the present invention. When the process is operated in accordance with the foregoing preferred method the rosin as delivered without vacuum distillation from still 25 is of marketable grade and of superior quality compared with the rosin heretofore produced by the solvent extraction of resinous woods. Grades above H are readily obtainable, and the product is moreover suited to certain uses, such as the manufacture of soap, high grade varnishes and paper size, for which the present wood rosins are not well suited.

Also the rosin may be vacuum distilled in order to produce the highest grades. In case it is desired to subject the rosin remaining in the rosin still 25 to a vacuum distillation, the valve 34 in line 35 leading to condenser 27 is closed, and valve 36 in line 37 leading to pure rosin receiver 38 is opened. Receiver 38 is connected with vacuum pump 28 by means of valve 39 in line 40, which is then opened. The temperature in the oil coil 33 is then raised a sufficient amount over 280° C. to sufficiently distill the rosin residue from still 25 over to the receiver 38, the desired reduction of pressure being maintained therein through the open system by means of the vacuum pump 28.

I have further discovered that the rosin produced by this process can be refined by vacuum distillation to yield the highest grade X.

As previously stated, it is possible by means of a solvent containing butane, or its equivalent in use, to secure a very rapid extraction. While extractions can be made at ordinary temperatures, it is advantageous to employ a moderate degree of heat. For this purpose the extraction battery as shown may be equipped with interstage heating units as above mentioned. The recommended temperature range may be between 50° and 100° C., but this range may be extended for some purposes, depending upon the conditions of the material operated upon and the qualifications of the solvent in use. Under some conditions it may be desirable to resort to higher temperatures. As a rule, the higher the temperature the more rapid and complete is the extraction. Use of higher temperatures than 100° C. is recommended to be avoided. At 50° C. the working pressure for the butane fraction, which is recommended, is of the order of 60 to 70 pounds; at 75° about 120 pounds. The time required for the extraction depends upon the size of the wood, whether chips or shredded wood, the circulation and the temperature. With good circulation and chips of ½″ mean size a period of 1½ hours will be substantially effective for each extraction stage, but it will be understood that longer periods of extraction for chips of larger size may be resorted to without detriment, leaving the wood in good condition for paper manufacture. The time for extraction necessarily varies with the condition of the material to be extracted, but is substantially shorter than usual treatments of which I am aware.

As an example of yields, the following results of practice can be cited:

Yields per ton of stump wood (long-leaf yellow pine)

Rosin	410 pounds
Turpentine	6.3 gallons
Pine oil	3.3 gallons

It is thus apparent that I have provided a novel process particularly adapted to the efficient extraction of resins from woods and producing an extracted chip wholly suitable for use in paper manufacture; various novel intermediate products and wood rosins of high grades suitable for uses not available for wood rosins heretofore produced.

When the process is carried out on moist or damp wood chips, the water substantially remains entrained with and is removed with the extracted wood. From time to time the circulating solvent may be treated to remove water in solution, for example by subjecting the solvent in gaseous or liquid state to a water-freezing temperature and removing the ice formed.

The examples of practice and product hereinabove described are offered by way of illustration and exemplification of the invention and not by way of limitation, and variations of practice and different products are contemplated within the definitions of the appended claims.

I claim:

1. Process for the treatment of coniferous woods to recover therefrom hydrocarbon soluble extractives which comprises the step, subjecting such woods to extraction in a liquid hydrocarbon solvent of low average molecular weight, said solvent having a vapor pressure at 75° C. in excess of 1000 and less than 20,000 mm. of mercury under conditions of time, temperature and pressure suitable for the solution of said extractives, during maintenance of the solvent in liquid phase.

2. Process for the treatment of coniferous woods to recover therefrom hydrocarbon soluble extractives which comprises subjecting chips of such woods to immersion in a liquid hydrocarbon solvent having a molecular weight of less than 78 and more than 28 under conditions of time, temperature and pressure suitable for the solution of said extractives during maintenance of said hydrocarbon solvent in liquid phase.

3. Process for the extraction of coniferous woods to recover therefrom hydrocarbon-soluble extractives which comprises subjecting the wood to the solvent action of a nor-

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mally gaseous hydrocarbon solvent chiefly comprising butane and held liquid under pressure in a suitable vessel.

4. A process for the extraction of coniferous woods to recover therefrom hydrocarbon soluble extractives which comprises subjecting such woods while in a moist state to wetting with a normally gaseous hydrocarbon solvent chiefly comprising a mixture of butane and propane held liquid under pressure.

5. Process for the extraction of hydrocarbon soluble extractives comprising subjecting wood containing resinous bodies in a moist state to contact with a normally gaseous hydrocarbon solvent held in liquid phase and effective to dissolve the resinous bodies in the presence of water.

6. Process for the treatment of coniferous woods to recover therefrom rosin, turpentine and pine oil which comprises treating such woods during a sufficient time with a liquid hydrocarbon solvent of low average molecular weight, said solvent having a vapor pressure at 75° C. in excess of 1000 and less than 20,000 mm. of mercury under conditions of temperature and pressure suitable for the effective solution of the contained terpene and resinous contents and removing said extractives, the removal of said extractives ensuing without decomposition and without removal of discoloring impurities from the wood.

7. A process for the treatment of coniferous woods to recover therefrom hydrocarbon soluble extractives which comprises multiple countercurrent extraction in a closed system at temperatures between 50° C. and 100° C. and pressures suitable to maintain said solvent in liquid phase at said temperature said liquid hydrocarbon solvent being low average molecular weight, said solvent having a vapor pressure at 75° C. in excess of 1000 and less than 20,000 mm. of mercury.

8. A process for the treatment of coniferous woods to recover therefrom hydrocarbon soluble extractives which comprises treating such woods for a time of the order of from one to four hours with a hydrocarbon solvent comprising chiefly butane at temperatures between 50° and 100° C. under pressure.

9. A process for the treatment of coniferous woods to recover therefrom rosin, turpentine and pine oils which comprises treating such woods with a hydrocarbon solvent comprising chiefly butane at temperatures between 50° and 100° C. under pressure, separating the solvent and extractives from the woods, recovering the solvent from the extractives for re-use, distilling the residue to remove terpene oils from the rosin, and vacuum distilling the residual rosin.

10. A process for the treatment of coniferous woods to recover therefrom hydrocarbon soluble extractives which comprises treating such woods with a liquid hydrocarbon solvent of low average molecular weight, said solvent having a vapor pressure at 75° C. in excess of 1000 and less than 20,000 mm. of mercury under conditions of time, temperature and pressure suitable for the solution of said extractives, separating the solvent and extractives from the woods, recovering the solvent from the extractives for re-use, distilling the residue to remove terpene oils from the rosin, and vacuum distilling the residual rosin.

11. A process for the treatment of coniferous woods to recover therefrom rosin, turpentine and pine oils which comprises treating such woods with a hydrocarbon solvent comprising chiefly butane at temperatures between 50° and 100° C. under pressure, distilling the residue to remove terpene oils from the rosin and vacuum distilling the residual rosin.

12. Process for the extraction of naturally occurring solid inclusions in celulosic materials with normally gaseous hydrocarbon solvents having a vapor pressure at 75° C. in excess of 1000 and less than 20,000 mm. of mercury in a closed system under pressure comprising extracting said materials in an extraction unit, separating the solvent and solute from the materials, distilling a major portion of the solvent from the solute under pressure and condensing the solvent and returning it to the extraction unit under pressure, vaporizing the remaining solvent from the solute by reducing the pressure to strip the last traces of solvent from the solute, and condensing the recovered solvent and returning it to the extraction unit.

13. Process for the extraction of rosin from coniferous woods with a normally gaseous hydrocarbon solvent having a vapor pressure at 75° C. in excess of 1000 and less than 20,000 mm. of mercury, comprising extracting said materials in an extraction unit, separating the solvent and solute from the materials, distilling a major portion of the solvent from the solute under pressure and condensing the solvent and returning it to the extraction unit in a closed system under pressure vaporizing the remaining solvent from the solute by reducing the pressure to strip the last traces of solvent from the solute and condensing the stripped solvent under pressure sufficient to maintain the solvent in liquid phase during extraction of the material.

14. A process for the extraction of terpenes and rosins from coniferous woods with a hydrocarbon solvent, normally gaseous at extracting temperature, comprising extracting said terpenes and rosins in an extraction unit with a hydrocarbon solvent removing the solvent and extractives from the wood, distilling the solvent from the ter-

penes and rosins at a temperature below 100° C., condensing the solvent and returning it to the extraction unit in a closed system while maintaining a sufficient pressure in the system to keep the solvent liquid in the extraction unit, and flash vaporizing the solute terpene and rosin bottoms to strip the last traces of solvent therefrom by the retained heat of the solvent and solute liquid, condensing the recovered solvent and returning it to the extraction unit.

Signed by me at Cambridge, Massachusetts, this fourth day of October, 1927.

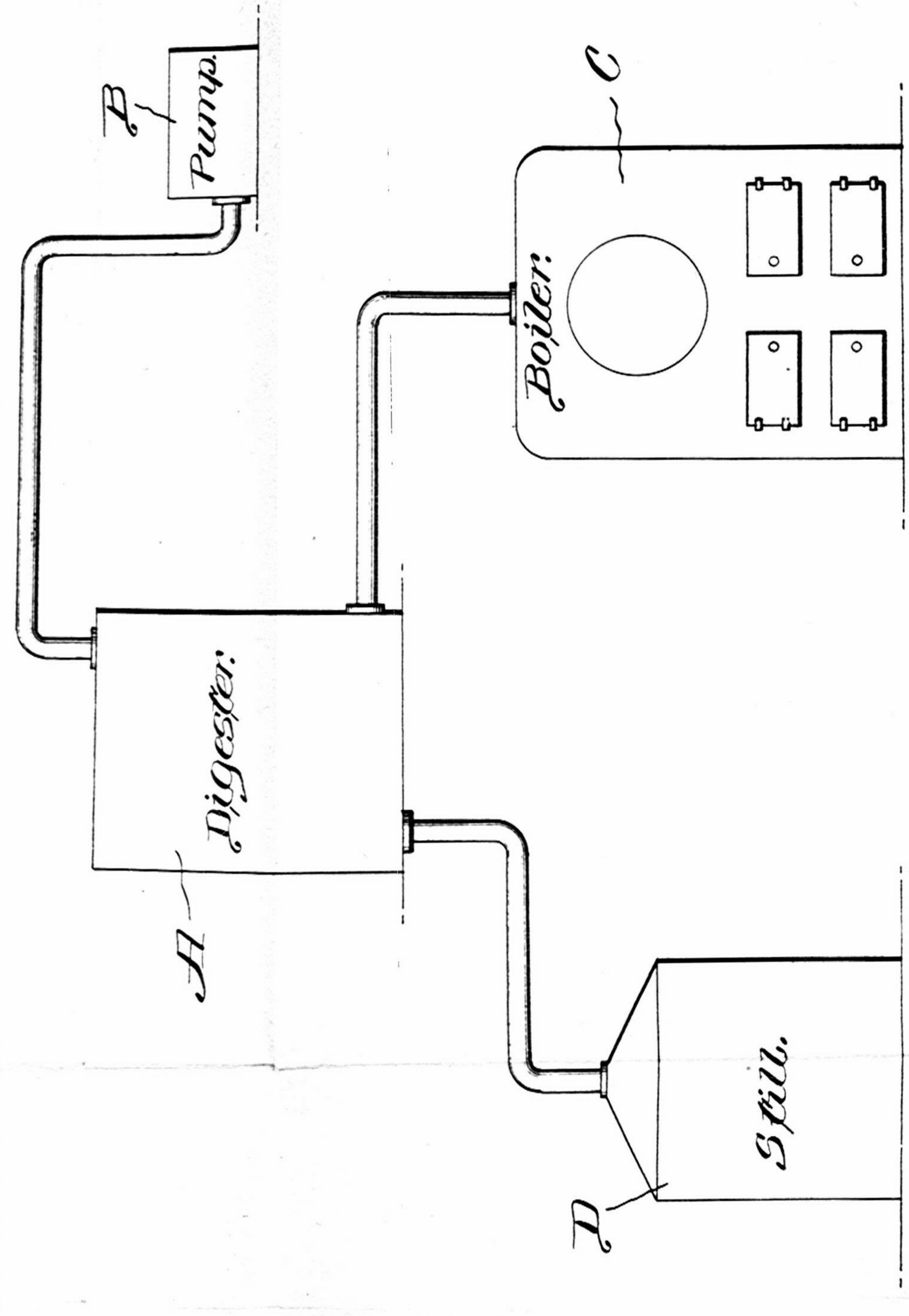
ARTHUR D. LITTLE.

I. S. CLOPE.

PROCESS FOR EXTRACTING FROM WOODS THEIR SOLUBLE CONTENTS.

APPLICATION FILED OCT. 22, 1913.

1,112,359. Patented Sept. 29, 1914.



Inventor
Irving Spencer Clope.
by Wilkinson, Giusta & Mackaye,
Attorneys

Witnesses
Edwin J. Beller.
H. W. Premm

UNITED STATES PATENT OFFICE.

IRVING SPENCER CLOPE, OF WILKINSBURG, PENNSYLVANIA, ASSIGNOR TO EMPIRE CHEMICAL COMPANY, OF ATLANTA, GEORGIA, A CORPORATION OF GEORGIA.

PROCESS FOR EXTRACTING FROM WOODS THEIR SOLUBLE CONTENTS.

1,112,359. Specification of Letters Patent. **Patented Sept. 29, 1914.**

Application filed October 22, 1913. Serial No. 796,678.

To all whom it may concern:

Be it known that I, Irving Spencer Clope, a citizen of the United States, residing at Wilkinsburg, in the county of Allegheny and State of Pennsylvania, have invented certain new and useful Improvements in Processes for Extracting from Woods Their Soluble Contents; and I do hereby declare the following to be a full, clear, and exact description of the invention, such as will enable others skilled in the art to which it appertains to make and use the same.

I have invented and discovered certain new and useful improvements in processes of extracting from resin bearing woods their resinous and other constituents.

My invention contemplates the extraction, from woods, particularly from coniferous woods, of the rosin, pine oil, turpentine, wood alcohol, acetone and water, with perhaps other ingredients, by means of the haloid derivatives of acetylene, ethylene and ethane. I may use one or any number of these derivatives. The particular one of these which I have found most useful, generally, is trichlorethylene. This is a compound, liquid which, at a steam pressure of 25 pounds, that is a temperature of 112° C., has no deleterious effect upon any of the usual metals. It has a boiling point of about 88° C., and a specific gravity of 1.47. It does not decompose at its boiling point, and its vapor has a very low tension and is non-inflammable.

The resinous constituents of pine, and similar woods, are very valuable, in some instances being much more valuable than the complete wood structure. Rosin and turpentine are particularly important products in this connection. Their extraction from the associated ligneous tissue has been attempted in many ways by the use of solvents, and many of these solvents will remove the constituents aforesaid to a considerable extent. Particularly is this true of the hydrocarbons, such as naphtha. The extractive qualities of the hydrocarbon solvents, however, are such that the products, particularly the rosin, is not of the grade that the market demands, nor as good as that obtained by the ancient method of "boxing" the trees. This is probably due to the fact that the two acids which constitute the bulk of commercial rosin, namely abietic acid and colophonic acid, are not equally soluble in such solvents, and the hydrocarbon dissolves first the softer and more readily soluble one of these acids, leaving the harder and more brittle rosin constituent behind in the fibers of the wood, to some extent at least. A solvent of the class I use, and particularly trichlorethylene, seems to dissolve with equal readiness both the acids of the rosin, as well as the other constituents of the wood that I have mentioned.

After treatment, the fiber, that is the cellulose and lignose of the wood, is left behind practically clean, and may be turned over at once if desired, to the pulp maker, or may be used in any other way that is desired.

After extraction, the solvent liquid, together with the bodies dissolved therein, is subjected to fractional distillation, whereby the acetone and wood alcohol are separated first, then the solvent, then the turpentine and pine oil and water, leaving the rosin behind in the still in the form of a dense, clear and clean mass. The solvent is, of course, recovered and used again.

The accompanying drawing is a diagram of an apparatus that may be used in carrying out my process, and in which A represents a digester or vessel; B a pump for exhausting said digester or vessel; C a boiler in which the vapors of the solvent are generated and from which they pass to the digester or vessel; and D a still in which the solvent and dissolved woody constituents are subjected to fractional distillation.

In carrying out my process I charge a digester or vessel with chips or billets of the wood undergoing treatment. The digester or vessel may then be exhausted of air, the vapor from the boiling solvent is let into the digester; the chips being practically free from air, the solvent vapor immediately penetrates the pores and intercellular spaces of the wood, and the solvent action begins at once. The fact that this penetration has occurred induces the subsequent penetration of the extracting vapors. As the vapors condense, they trickle down to the bottom of the digester charged with the dissolved constituents of the wood, and this liquid may be continuously withdrawn, or withdrawn from time to time, into a receiver and led to a still for further treatment. Condensation of substances of the class to which mine be-

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longs occurs readily, little heat being given off, so that it is not necessary to subject a charged digester to chilling influences during the extraction process. By this process of leading the solvent into the digester in the form of vapor and allowing it to condense among the chips it will be seen that the chips are at no time immersed in a liquid bath of the solvent and its dissolved extract, but that the chips are leached clean, as it were, of everything except the final charge of condensed solvent, in a manner well understood. However, instead of treatment with vapor *in vacuo*, the solvent may be used in the liquid form, the chips being either immersed therein, or the liquid solvent caused to flow through them. Or the treatment may be partly with the solvent in the liquid form, and partly with it in the form of vapor.

As I have indicated above, while my process is particularly intended for woods of coniferous genera, I do not desire or intend to be limited to the treatment of such woods, as the solvents of the group I have used, and particularly the particular solvent, trichlorethylene, is well adapted for the extraction of most of the constituents, except the cellulose and lignose of any wood.

Having thus described my invention what I claim and desire to secure by Letters Patent of the United States is:—

1. The process of extracting from coniferous woods, their soluble constituents, which consists in treating such woods with trichlorethylene.

2. The process of extracting from coniferous woods, acetone, wood alcohol, turpentine, pine oil and resin, which consists in treating such woods in a vacuum with vapors of trichlorethylene, allowing such vapors to condense, together with the dissolved constituents of the wood in such condensate, and subjecting the resulting solution thus formed to fractional distillation.

3. The process of extracting from coniferous woods, acetone, wood alcohol, turpentine, resin, and other soluble constituents, which consists in treating such woods with vapors of trichlorethylene, allowing such vapors to condense, together with the dissolved constituents of the wood and subjecting the resulting solution thus formed to fractional distillation.

In testimony whereof, I affix my signature, in presence of two witnesses.

IRVING SPENCER CLOPE.

Witnesses:
R. M. PARKER,
ERNEST WILLIAMS.

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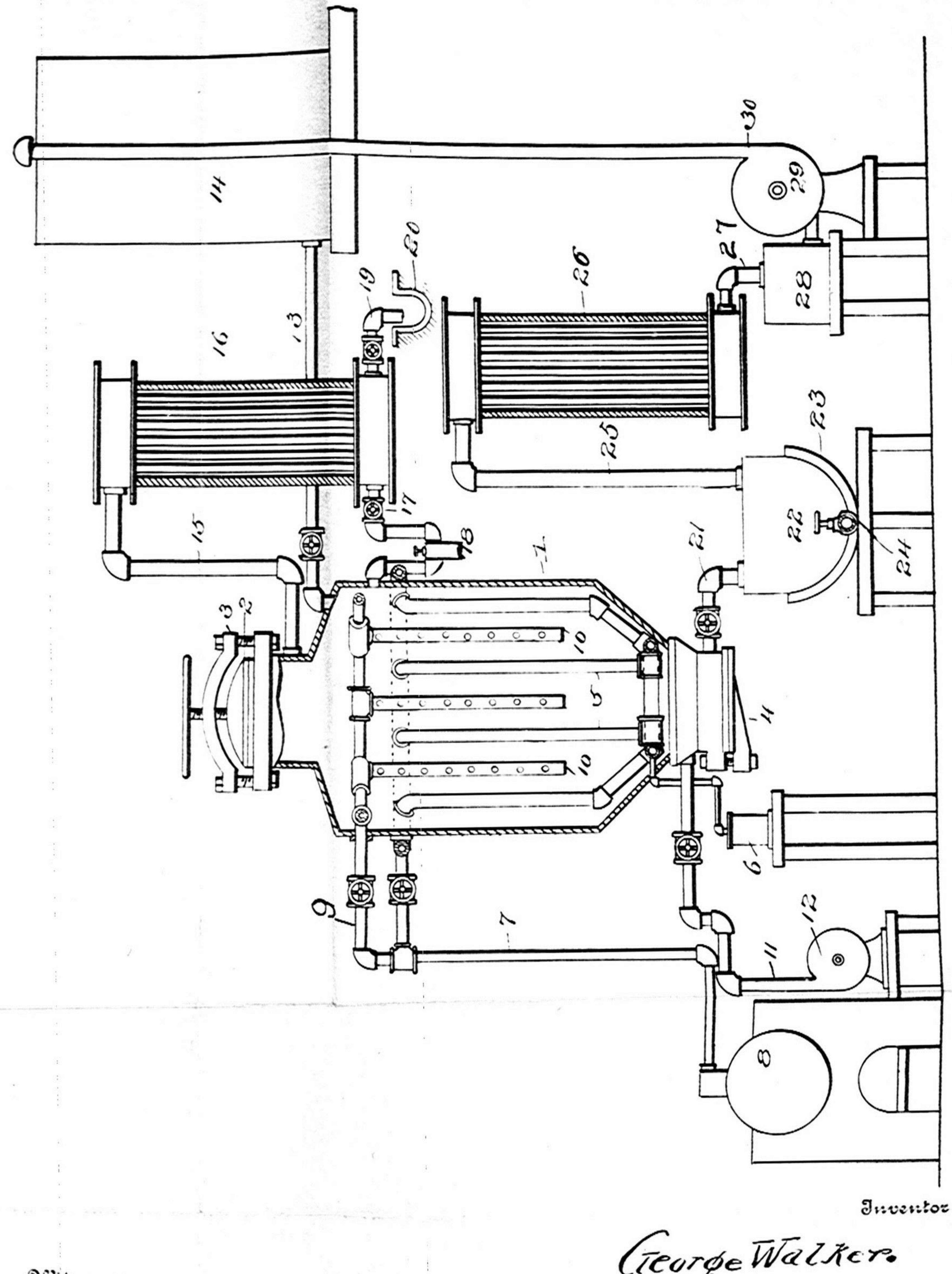
G. WALKER.

PROCESS OF EXTRACTING RESIN AND TURPENTINE.

APPLICATION FILED MAY 9, 1908.

922,369. Patented May 18, 1909.



Inventor

George Walker.

Witnesses

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UNITED STATES PATENT OFFICE.

GEORGE WALKER, OF NEW YORK, N. Y., ASSIGNOR TO HOMER T. YARYAN, OF TOLEDO, OHIO.

PROCESS OF EXTRACTING RESIN AND TURPENTINE.

No. 922,369. **Specification of Letters Patent.** **Patented May 18, 1909.**

Application filed May 9, 1908. Serial No. 431,757.

To all whom it may concern:

Be it known that I, George Walker, a citizen of the United States, residing at New York, in the county and State of New York, have invented certain new and useful Improvements in Processes of Extracting Resin and Turpentine, whereof the following is a specification.

This invention relates to processes of extracting resin and turpentine; and comprises a method of extracting turpentine and resin from coniferous woods in which such wood is first freed from turpentine, volatile terpenes, etc., by distillation under conditions injurious neither to the turpentine nor the resin and is subsequently extracted with a volatile solvent body to obtain a pure resin; all as more fully hereinafter set forth and as claimed.

In the prior art, coniferous wood has been directly extracted with various solvents, hydrocarbons being generally employed, to obtain rosin and turpentine at one operation. The extract obtained contains both bodies, together with the solvent employed, and is distilled to remove, first the solvent and then the turpentine, the rosin being left behind in the still as a residue. This method however suffers from a number of disadvantages and does not give rosin and turpentine of good commercial grades. The turpentine is generally ill-smelling, partly because of bodies derived from the solvent employed, and partly, no doubt, because of the presence of wood constituents or products other than turpentine, while the rosin generally suffers in clearness, color and quality by the repeated distillations necessary to free it of the solvent employed and of turpentine, a high temperature being usually employed in such distillations. Rosin does not well withstand long continuance of high temperatures. Since even volatile commercial hydrocarbons like gasolene and naphtha, contain high-boiling impurities such impurities tend to contaminate the turpentine.

In the present process I have devised a simple, cheap and ready method of preparing a pure rosin and turpentine of good commercial grades, this method obviating the stated disadvantages and securing certain new advantages. According to this invention, I preliminarily treat the wood, which may be any of the coniferous woods, by a distillation at comparatively low temperatures, that is, temperatures at which neither the woody fiber nor the resin will suffer pyrolytic decomposition or injurious changes and afford decomposition products to contaminate the distillation product. This distillation gives me turpentine, leaving the rosin in the wood unchanged. While the distillation may be effected by simple heating of the comminuted wood in thin layers, or strata, since wood contains considerable water which in evaporating carries the turpentine with it, yet in practice it is better to use some form of gaseous or vaporous carrier. Under the ordinary laws of evaporation, turpentine evaporates much more freely and at a lower temperature into a gas mass carrying little of its own vapors than into a gas mass containing much of such vapors, so that it is desirable to use a considerable volume of a gaseous or vaporous carrier circulating past the wood being distilled and absorbing and diluting the turpentine vapors as fast as formed. Air or neutral gases may be employed, the latter being better since air oxidizes turpentine and rosin, but steam is still better. I therefore preferably conduct the distillation by passing steam past or through the wood under treatment. The higher the temperature and pressure of the steam the quicker the distillation may be effected, but steam under 10—20 pounds pressure is perfectly suitable and is especially adapted to the present purposes while still lower pressures and the concomitant temperatures may be employed. With steam of low temperature, while the turpentine distills over well, the rosin is not damaged. At temperatures approaching or above the boiling point of turpentine, while the turpentine may be removed by the use of very little steam, yet the rosin is apt to be injuriously affected and to yield more or less rosin oil to contaminate the turpentine.

The wood is preferably finely comminuted, in the form of sawdust or small chips, such as, for example, those given by the "sawmill hog." It may be distilled in thin layers or strata, stationary or moving, but when steam is employed, the use of such thin layers or strata is not necessary and the comminuted wood may be in substantial masses of sawdust or chips and be contained in any suitable vessel. Preferably however, to save labor and expense, this vessel is the same as that subsequently employed for extraction. Using steam, low pressure steam is blown through or past the mass of wood to and through a condenser of any ordinary type wherein it condenses together with the turpentine vapors which it carries, the condensed water and turpentine being then gravitally separated. The passage of steam and the distillation are discontinued when the condensate no longer separates substantial quantities of turpentine. The distilled wood, thus freed of turpentine and containing the residual rosin in a substantially unchanged state, is next extracted with a volatile solvent capable of dissolving rosin. While the number of possible solvents which may be here employed is very large, almost any of the ordinary "volatile solvents," that is, any of the ordinary, low-boiling, chemically neutral solvents, such as grain or wood alcohol, petroleum hydrocarbons, like gasolene, benzin or naphtha, ether, methyl or ethyl acetate, benzol, acetone, etc., being all more or less adapted for this purpose, I prefer to use a special distillate from hard wood tar as free from disadvantages for this purpose inherent in most of the other common solvents. Petroleum hydrocarbons, for instance, while freely dissolving certain constituents of commercial rosin (from gum turpentine) do not dissolve other constituents so freely. Consequently in treating the wood with a limited quantity of gasolene, for instance, the solvent extracts more of certain resinous constituents of the wood than of other constituents, and the resinous matter regained on evaporating the extract is not the same as rosin from gum turpentine.

In destructively distilling hard woods, the condensate contains many and different substances, the aqueous portion or "pyroligneous acid" containing besides acetic acid, acetone, methyl alcohol and water a considerable portion of oily bodies held in solution and suspension by the influence of the solvent bodies named while the non-aqueous portion, or tar, contains a still larger amount of these oily bodies. In purifying the pyroligneous acid these oily bodies may be regained and the oily bodies may also be produced by direct distillation of the tar. Certain fractions of the oily bodies from either source may be employed in the present invention. Using hard wood tar, the tar is distilled in a suitable still till about half its weight passes over, the temperature of distillation being between 100° and 250° C. The first half of the distillate will consist of pyroligneous acid containing some wood spirit and of an oil lighter than water though containing some high-boiling heavy oils codistilled therewith. The oil and acid are gravitally separated and the oil is next washed with water and with alkali to free it from acid and creosote and phenolic bodies and render it neutral. It is then redistilled in any suitable fractionating still to obtain the low boiling fractions, the fractions between 65° C. and 100° being particularly suitable for the present purposes though the fractions up to 170° C. may be employed. The distillate is of course neutral, the acids and phenolic bodies having been removed by the alkali. Any caustic alkali may be used, but soda or lime are suitable.

The oily bodies obtained in purifying pyroligneous acid by any of the ordinary methods are substantially the same as those obtained from wood tar and may be treated in the same manner as above indicated for the distillate from tar.

After steam distilling wood and before extracting with a solvent, the wood is preferably dried by any suitable method to permit good extraction since water-immiscible solvents do not well penetrate the damp fiber generally left by the treatment with low pressure steam while water-miscible solvents, such as alcohol, in taking up moisture lose much of their solvent power for rosin. Such drying is not absolutely necessary but it economizes in time and quantity of solvent employed. A convenient method is to follow the steam used in removing turpentine, etc., with a blast of air, supplying some heat at the same time, either by heating the air or the wood.

In the accompanying illustration I have shown, more or less diagrammatically, certain types of apparatus of the many adapted for use in the described process. In this showing, the figure represents, partly in central vertical section and partly in elevation, a simple type of apparatus (chosen for illustration because of its simplicity) in which the preliminary distillation and the subsequent extraction are performed in the same vessel, but one such vessel being shown. In practice, however, a plurality of similar vessels will generally be employed, connected in well understood ways to permit a methodical use of the same portion of solvent on a plurality of portions of distilled wood in the same manner as in diffusion batteries, thereby obtaining concentrated solutions and economy in the use of solvent. In this figure, 1 is the extraction and distillation vessel, provided with removable cover 2 secured by clamping means 3. At its base, the vessel is provided with door 4. Internally the vessel is provided with steam heating means, shown as steam pipes 5 placed near the sides. At their base, they communicate with steam trap 6. Steam is furnished by steam main 7 from boiler 8. Another connection 9 from the steam main furnishes steam to a series of perforated steam pipes 10 or other suitable means for introducing live steam within the vessel. Pipe 11 connected to fan 12 allows the introduction of an air blast at the bottom of the vessel. Near the top of the vessel is pipe 13 allowing the introduction of rosin solvent from storage tank 14 while above it is vapor main 15 passing to condenser 16 of an ordinary type. At its base, this condenser is provided with a valved return pipe 17 trapped at 18, to permit return of condensates to the extraction vessel. It is also provided with another valved outlet pipe, 19, shown as discharging into gutter or conduit 20 for water and turpentine. Communicating with the base of the extraction vessel is a valved extract pipe 21 leading to rosin still 22. This still is shown as steam heated, being provided with steam jacket 23, and has an outlet 24 for melted rosin. From the rosin still leads vapor pipe 25 to condenser 26 for the recovery of solvent. At its base, the condenser has discharge pipe 27 leading to tank 28 from which pump 29 withdraws condensed solvent and discharges it through pipe 30 to the storage tank for reuse.

In the operation of the apparatus shown and in performing the described process, the wood employed, which may be pine, light wood or any other form of coniferous wood, in a comminuted form, as sawdust, chips, "hogged wood," etc., is charged into the distillation and extraction vessel and is subjected to a blast of steam from pipes 10. Heating may be assisted by steam in coils 5. The steam, both that introduced and that formed from the moisture in the wood, passes outward through vapor main 15, carrying with it the volatilized turpentine. Water and turpentine are condensed in 16 and delivered through 19 into 20, 20 delivering the condensate to any suitable containing vessels (not shown). When no more substantial amount of turpentine is found in the condensate, the direct steam is turned off, the cover of the vessel removed and air blown through the wood to dry it and remove the steam and moisture. Drying may be hastened and facilitated by continuing the heating by steam coils 5 during the passage of the air. Hot air may be employed, but is hardly necessary since the coils furnish heat more conveniently. The first portions of air going through which will generally carry some steam and turpentine, may be sent to the condenser, but this is usually hardly worth while.

When the wood is sufficiently dry and free of steam, the introduction of air is discontinued and sufficient solvent to cover the wood is introduced through pipe 13 from storage tank 14. This solvent is preferably the neutral volatile hardwood tar distillate described, but it may be another neutral volatile solvent. In contact with the hot wood, the solvent is raised to the boiling temperature and it is preferably maintained at this temperature by the steam coils 5, extraction being better at high temperatures. Such solvent as volatilizes passes out through vapor main 15, is condensed in 16 and returns to the extractor through 17, the valve of pipe 19 being closed. After contact with the wood for a sufficient time, the charged solvent or rosin solution may be drawn off through 21 and sent to rosin still 22. Any rosin which, in the case of such resinous materials as "light wood," may have trickled down to the floor of the vessel during the steam distillation is dissolved by the solvent during the extraction and passes outward through 21 with the first portions of rosin solution. After withdrawal of the first portion of solvent, another portion of fresh solvent, or solvent which has been previously used elsewhere, may be introduced if desired.

When the extraction is completed, as many portions of solvent having been used as may be desired (and the portions may be used methodically in a plurality of vessels as stated, if so desired), the solvent remaining adhering to the wood is removed by passing in a little steam which volatilizes it, the vapors being allowed to pass through 15 into 16 and removed as liquid at 18, or following the liquid extract, to pass through 21 into 22, thence through 25, 26 and 27 into 28. Having removed the solvent, the lower door of the extraction vessel is opened and the exhausted wood dumped, leaving the vessel ready for another operation. The exhausted wood may be used for paper making or burned as fuel. The rosin solution in still 22 is distilled, the solvent being condensed and regained for future operations. The melted rosin remaining in the still is removed through 24.

The described low-boiling hardwood tar distillate is well adapted for extracting other valuable resins from wood as well as for extracting rosin.

By separately extracting the turpentine and resin in the manner described, the quality of each is improved. In extracting them together from the wood by solvents, as in the prior art, a mixture of solvent, turpentine and the resin, such as rosin, is obtained from which solvent and turpentine must be fractionated. As turpentine boils at a comparatively high temperature, in removing the last fractions of the turpentine from such a mixture there is apt to be some decomposition of the rosin, forming rosin oils which mix with the turpentine, injuring the quality of the rosin. And, in using the petroleum oils as solvents, the turpentine is apt to be contaminated with high-boiling impurities therefrom. The rosin itself is apt to be injured by the prolonged heating at high temperatures in removing the solvent and turpentine, darkening in color. And, as stated, when removed from the wood by hydrocarbons, it is apt to be different in composition from ordinary rosin. The described neutral tar distillate on the other hand gives a good quality of rosin.

While when employing the described low-boiling hardwood tar distillate as a solvent, both turpentine and resin can be simultaneously extracted, yet I regard it as preferable to extract them successively in the manner described, first distilling off the turpentine and then using the solvent.

The volatile solvents stated, like all those generally classed under that name, are neutral bodies; that is, chemically indifferent toward acid and alkali. This characteristic, and particularly the indifference toward acid, is valuable for the present purposes since alkaline-reacting bodies would tend to combine with the resin acids to form soapy bodies whence they could be removed only with difficulty.

What I claim is:—

1. The process of extracting turpentine and rosin from wood which comprises distilling off volatile bodies from a resinous wood at a temperature insufficient to injure the rosin, and subsequently extracting the wood with a neutral volatile solvent to remove rosin.

2. The process of recovering turpentine and rosin from wood which comprises distilling off turpentine from resinous Rood in a current of steam at a temperature below the boiling point of turpentine and subsequently extracting the wood with a neutral volatile solvent to remove rosin.

3. The process of recovering turpentine and rosin from wood which comprises distilling off turpentine from resinous wood in a current of steam at a temperature below the boiling point of turpentine, drying the wood to remove the steam and subsequently extracting the wood with a neutral volatile solvent to remove rosin.

4. The process of recovering valuable products from coniferous woods which comprises extracting such woods with a neutral low-boiling distillate from hardwood tar.

5. The process of recovering turpentine and rosin which comprises distilling off turpentine from a resinous wood in a current of low pressure steam and subsequently extracting rosin from the wood with a neutral low-boiling distillate from hardwood tar.

6. The process of recovering turpentine and rosin which comprises distilling off turpentine from a resinous wood in a current of low pressure steam, drying the wood to remove the steam and subsequently extracting the wood with a neutral low-boiling distillate from hardwood tar.

7. The process of recovering valuable products from wood which comprises placing such wood in a suitable container, distilling off volatile bodies from such wood in the presence of aqueous vapor at a low pressure and temperature, removing such vapor from container and wood, and extracting the wood remaining in such container with a neutral volatile solvent.

8. The process of recovering valuable products from resinous wood which comprises placing such wood in a suitable container, distilling off turpentine in the presence of aqueous vapor at a low pressure and temperature, removing such vapor from container and wood and extracting rosin from the wood remaining in the container with a neutral volatile solvent.

9. The process of recovering rosin from wood which comprises placing comminuted resinous wood in a suitable container, distilling off turpentine and volatile bodies in a current of steam at a temperature below the boiling point of turpentine, removing steam and moisture from the wood in said container, extracting the rosin from the treated wood with a neutral volatile solvent and recovering the rosin from the rosin solution so formed.

10. The process of recovering turpentine and rosin from wood, which comprises distilling off turpentine from resinous wood in a current of steam at a temperature below the boiling point of turpentine, the passage of said steam being continued until substantially no more volatile products are carried over thereby, and subsequently extracting the wood with a neutral volatile solvent to remove rosin.

In testimony whereof I affix my signature in the presence of two subscribing witnesses.

GEORGE WALKER.

Witnesses:
WILLIAM E. REILLY,
FRANCES FORESTER.

Correction in Letters Patent No. 922,369.

It is hereby certified that in Letters Patent No. 922,369, granted May 18, 1909, upon the application of George Walker, of New York, N. Y., for an improvement in "Processes of Extracting Resin and Turpentine," an error appears in the printed specification requiring correction, as follows: In line 26, page 4, the word "Rood" should read *wood;* and that the said Letters Patent should be read with this correction therein that the same may conform to the record of the case in the Patent Office.

Signed and sealed this 8th day of June, A. D., 1909.

[SEAL.]

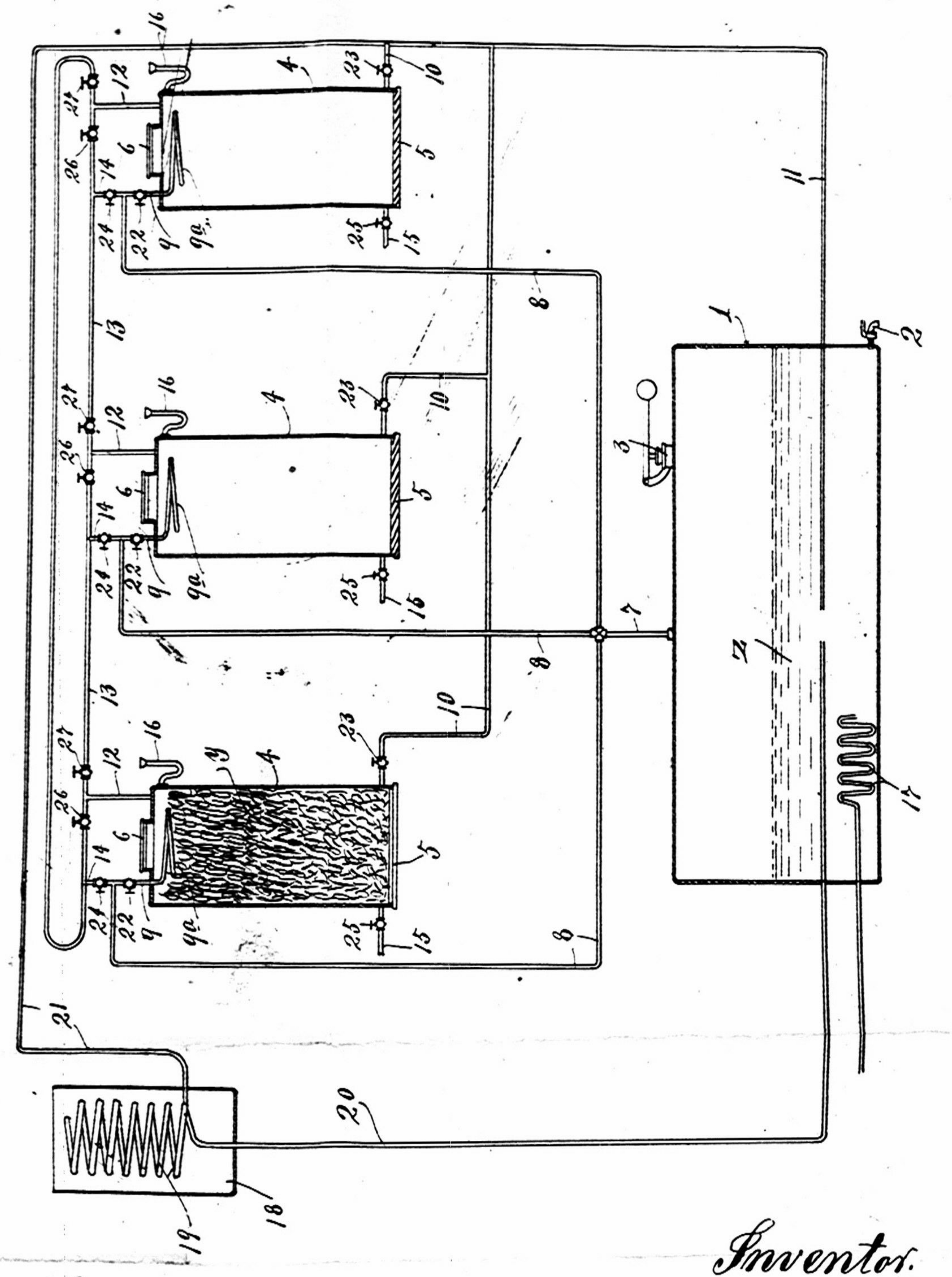
C. C. BILLINGS,
Acting Commissioner of Patents.

G. B. FRANKFORTER.

PROCESS OF EXTRACTING TURPENTINE AND RESINOUS MATTER FROM WOOD.

APPLICATION FILED JULY 13, 1906.

918,990. Patented Apr. 20, 1909.



Witnesses
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By his Attorneys
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UNITED STATES PATENT OFFICE.

GEORGE B. FRANKFORTER, OF MINNEAPOLIS, MINNESOTA.

PROCESS OF EXTRACTING TURPENTINE AND RESINOUS MATTER FROM WOOD.

No. 918,880. **Specification of Letters Patent.** **Patented April 20, 1909.**

Application filed July 13, 1906. Serial No. 326,085.

To all whom it may concern:

Be it known that I, George B. Frankforter, a citizen of the United States, residing at Minneapolis, in the county of Hennepin and State of Minnesota, have invented certain new and useful Improvements in Processes of Extracting Turpentine and Resinous Matter from Wood; and I do hereby declare the following to be a full, clear, and exact description of the invention, such as will enable others skilled in the art to which is appertains to make and use the same.

My invention has for its object to provide an improved process of extracting turpentine and resinous matter from resinous wood, and to this end it consists of the novel treatment and sequential steps of treatment hereinafter set forth and defined in the claim.

In carrying out this improved process, the wood is preferably first cut into small particles and may be in the form of saw-dust, shavings, "excelsior", or chips. The wood may be cheaply and practically reduced to chip form by running the same through what is known in saw mill parlance as a "hog".

The wood to be treated by the process is placed within a suitable containing vessel, hereinafter designated in the description of the apparatus as an "extraction chamber", and it is subjected to the action of one of the carbon compounds, such as ether, petroleum ether, or carbon disulfid, which has the property of dissolving and holding in solution the turpentine and resinous matter of the resinous wood.

The solvent liquid charged with turpentine and resinous matter held in solution thereby, is drawn off from the wood into a suitable containing vessel hereinafter designated in the description of the apparatus as a boiler, and by a low boiling temperature, insufficient to boil the turpentine and resinous matter, the solvent liquid is vaporized and is returned to the extraction chamber, while the turpentine and resinous matter are deposited in the boiler, from which boiler said turpentine and resinous matter may be drawn off from time to time.

After the turpentine and resinous matter have been extracted from the wood and carried from the extraction chamber by the solvent fluid, a very considerable amount of solvent fluid will remain in said extraction chamber; and in order to reclaim and save such portion of the solvent fluid, I introduce into said extraction chamber a so-called "reclaiming fluid". This reclaiming fluid must have a density which is different from that of the solvent fluid, and it must be of such nature that it will not permanently commingle therewith. To secure the best results, the said reclaiming fluid should be one whose density at the temperature at which reclamation or separation takes place, is greater than that of the solvent fluid, so that the latter will be caused to rise to the top of the extraction chamber and may be caused to pass out of an opening in the upper portion of said extraction chamber. To illustrate more clearly, suppose that petroleum ether, whose specific gravity is .67 and whose boiling point is about 55 degrees C., is used as a solvent fluid, and that water at a temperature above the boiling temperature of said solvent fluid is used as a reclaiming fluid. Under the treatment just described, the solvent fluid is converted into vapor and, hence, is caused to free itself from the wood particles, so that it may rise in the extraction chamber above the reclaiming fluid. Again, suppose that carbon disulfid, whose gravity is 1.29, and whose boiling point is about 47 degrees Cent., is used as a solvent liquid, and that hot water is used as a reclaiming fluid. In this instance the solvent fluid is of greater density than the reclaiming fluid at temperatures below 47 degrees Cent., but above 47 degrees Cent. the said solvent fluid, to-wit, the carbon disulfid, will be vaporized and the density of this vaporized carbon disulfid is less than that of the reclaiming fluid (the water), and as is evident, in this instance, the reclamation or separation of the solvent fluid from the reclaiming fluid takes place at or above the boiling temperature of the said solvent liquid, to-wit, the carbon disulfid.

When water is used as a reclaiming fluid, the wood from which the turpentine and resinous matter is extracted will remain intact and no material change will take place in the structure of the wood fiber.

The process above described, while independent of apparatus may, nevertheless, be economically carried out on a commercial scale by means of an improved apparatus disclosed and claimed in a companion application filed by me of date July 13, 1906, Serial No. 326,084, entitled "Apparatus for use in extracting turpentine and resinous matter from resinous wood". The said apparatus is herein illustrated and described for the purpose of illustrating more clearly the manner in which the improved process herein claimed may be economically carried out on a large scale.

The said apparatus is illustrated in the single view of the drawing.

Referring to the drawing, the numeral 1 indicates a large tank preferably horizontally disposed and constructed of steel, and which, on account of one of the functions which it performs, and for the sake of definiteness in the description of the apparatus, I designate as a boiler. This boiler 1, as shown, is provided at or near its bottom with a draw-off cock or faucet 2, and at its top is provided with a safety valve 3 of the usual or any suitable construction.

Located above the boiler 1 is a plurality of so-called "extraction chambers" which are adapted to contain the wood or resin containing material. As shown, these extraction chambers 4 are in the form of upright metal drums and they are provided with detachable bottoms 5 and removable upper end caps 6, which parts 5 and 6 may be detachably secured by means of threaded engagement, or by any other of the well known means for detachably securing such parts.

Vapor delivery pipes 7, 8 and 9 connect the upper portion of the boiler 1 with the upper portions of the several extraction chambers 4. The pipes 9 terminate, within the respective extraction chambers, in annular perforated spraying coils 9^a. Return pipes 10 and 11 connect the lower or bottom portions of the several extraction chambers 4 with the lower portion of the boiler 1. Outlet pipes 12 lead upward from the top of the several extraction chambers 4 and these outlet pipes 12 are connected by an endless pipe 13. In the drawing, the several extraction chambers 4 are shown as located in a row, but in practice they might be placed in circular arrangement and, of course, any desired number of the said extraction chambers may be employed. The short pipe sections 14, as shown, connect the endless pipe 13 to the several pipes 9. Pipes 15 open into the lower portions of the several extraction chambers 4, for a purpose which will hereinafter appear. Bent tubes 16 open to the atmosphere in the upper portions of the several extraction chambers 4. These tubes, when partly filled with water or other heavy liquid, constitute water traps or seals that are normally closed.

As a means for heating the contents of the boiler 1, a closed steam conveying coil leads from a suitable source of steam supply 17 and extends along the inner lower portion of said boiler.

The numeral 18 indicates an elevated water-containing tank which is adapted to be supplied with cold water by any suitable connections, (not shown). Within this tank 18 is a condensing coil 19, and to the lower end of which, as shown, are connected two pipes 20 and 21. The pipe 20 leads downward and terminates in the lower portion of the boiler 1, while the pipe 21 is directly connected, as shown, to one of the pipes 10 and hence is indirectly connected to all of said pipes 10 and to the pipe 11. Any vapor delivered into the coil 19 from the pipe 21 will be condensed and will run back into the boiler 1, through the pipe 20.

For purposes which will hereinafter appear, the several pipes are provided with valves located as follows: Each pipe 9 is provided with a valve 22; each pipe 10 is provided with a valve 23; each pipe 14 is provided with a valve 24; each pipe 15 is provided with a valve 25; and the continuous pipe 13 is provided with valves 26 and 27. The valves 26 and 27 are located one at each side of each of the outlet pipes 12.

The wood in the form of chips, shavings, excelsior or saw-dust is, of course, placed in the respective extraction chambers, while the tops 6 thereof are removed and while the bottoms 5 thereof are secured in position. The preferred manner for carrying out the improved process by means of the apparatus above described is as follows: One of the extraction chambers 4, let us assume the one at the left as shown in the drawing, is first filled with the wood particles and the boiler 1 is partly filled with the solvent liquid, which we will assume to be petroleum ether which is a low boiling hydro carbon compound having the property of dissolving and holding in solution turpentine and resinous matter. We will now assume that all of the valves 24, 25, 26 and 27 are closed, that the valves 22 and 23 of the said first extraction chamber at the left are opened, and that all other of the valves 22 and 23 are closed. We will now assume that the solvent fluid *z* in the boiler 1 is heated to a temperature sufficient to vaporize the said solvent liquid which, if the same be petroleum ether, requires a temperature above 55 degrees C. The solvent vapor generated in the boiler 1 will pass upward through the pipe 7 and through the left hand pipes 8 and 9 and spraying coil 9^a, and will be discharged into the left hand extraction chamber 4 and directly upon the wood particles *y* confined in said extraction chamber. The vaporized solvent fluid upon cooling will condense within the said extraction chamber 4 and will trickle down upon the wood particles and will dissolve and take into solution the turpentine and resinous matter thereof, and from said extraction chamber will flow back through the left hand pipe 10 and the return pipe 11 into the boiler 1. By the steam coil 17 or other suitable means, the temperature of the liquid within the boiler 1 is kept above the boiling temperature of the said solvent liquid, so that the said solvent liquid is continuously vaporized and caused to travel the course just described, through the extraction chamber noted and through the wood particles contained therein, and thence back to the boiler. The solvent liquid is revaporized by a temperature which is insufficient to vaporize either the turpentine or the resinous matter and, hence, the said turpentine and resinous matter is continuously deposited in the bottom of said boiler, from which boiler it may, from time to time, be drawn off through the faucet 2.

After the extraction of the turpentine and resinous matter from the wood contained in the said extraction chamber at the left, the valves 22, 23, 24 and 26 adjacent thereto, should be closed and the valves 25 and 27 adjacent thereto should be opened and also the valves 26 of the second or intermediate extraction chamber should be opened up. The opening of the valve 25 will permit the reclaiming fluid, which we will assume to be water, to run into and fill the said first or left hand extraction chamber, thereby forcing the lighter solvent fluid out of the said first extraction chamber and into the second or intermediate extraction chamber. In this way, the solvent fluid left in the first extraction chamber, after the extraction of turpentine and resinous matter from the wood has been completed, is not only reclaimed and saved, but is forced into the second extraction chamber. In practice, the so-called "second" or intermediate extraction chamber should be filled with the wood particles while the extraction of turpentine and resinous matter from the wood contained in the first extraction chamber is taking place.

The crooked tubes 16 which constitute a sealing device and which normally contain water or other liquid, are preferably made of glass, so that the operator can tell, by observing the upward movement of the liquid in said tube, when the extraction chamber has been filled with the water or other reclaiming fluid. After the first or left hand extraction chamber has been filled with the reclaiming liquid, and the solvent liquid has been forced out of the same, the valve 27 thereof should be closed to prevent the backward flow of the said solvent liquid. The said reclaiming liquid may be drawn off from the extraction chamber by any suitable device as, for instance, by allowing it to run backward through the pipe 15; or it may be removed from the said extraction chamber together with the wood particles, when the bottom 5 of the said chamber is removed.

The above arrangement, as is evident, makes it possible to continuously carry out the process of extracting the turpentine and resinous matter by always rendering available for use at least one of the extraction chambers.

Any of the solvent liquid which may be converted into vapor within any of the pipes 10 or 11 may rise through the pipe 21 into the open coil 19 where it will be condensed and from thence may run back to the boiler 1 through the pipe 20.

With the apparatus above described, it is possible to have two or more of the extraction chambers in action at one time. Before the faucet 2 is opened up to draw off the turpentine and resinous matter, it is advisable first to close the valves 23 in the return pipes and to open the valves 22 in the supply pipes 9, and by the application of heat to the contents of the boiler 1 to vaporize the solvent liquid and drive the same from the boiler into the extraction chambers.

What I claim is:

The process of extracting turpentine and resinous matter from resinous wood by means of a solvent fluid, and in reclaiming the solvent fluid after extraction has been completed, which consists in subjecting the wood to a solvent fluid and thereafter applying to said solvent fluid a reclaiming fluid in liquid condition but at a temperature above that of the boiling point of said solvent, whereby the said solvent is vaporized and removed from the wood and reclaiming fluid.

In testimony whereof I affix my signature in presence of two witnesses.

GEORGE B. FRANKFORTER.

Witnesses:
Malie Hoel,
F. D. Merchant.

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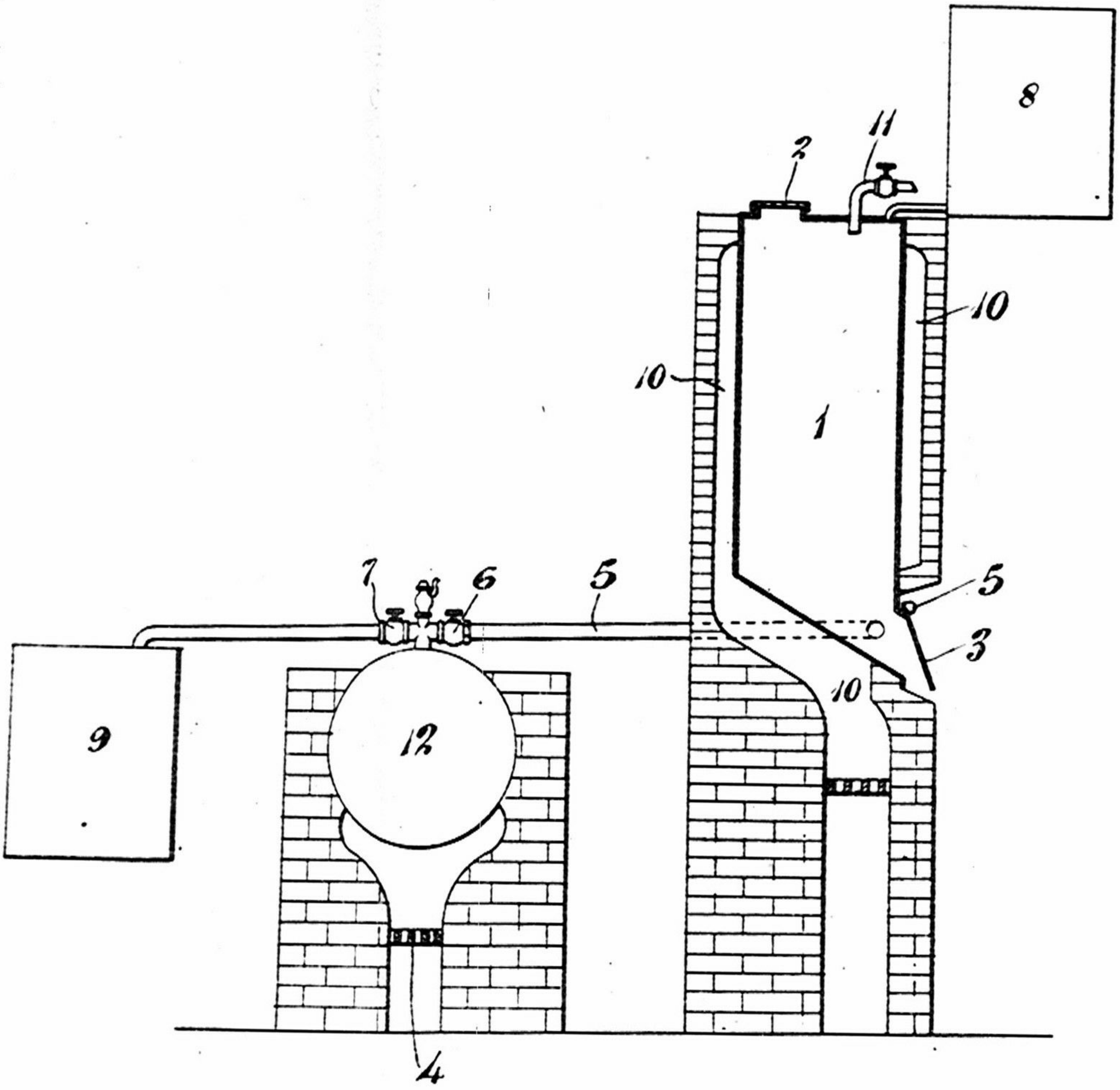
D. J. OGILVY.

PROCESS OF EXTRACTING RESINS, OLEORESINS, OILS, AND TURPENTINES FROM RESINOUS WOODS.

APPLICATION FILED SEPT. 10, 1912.

1,264,551. Patented Apr. 30, 1918.



Witnesses

Katherine Smith

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David J. Ogilvy

by Alfred M. Allen

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UNITED STATES PATENT OFFICE.

DAVID J. OGILVY, OF CINCINNATI, OHIO.

PROCESS OF EXTRACTING RESINS, OLEORESINS, OILS, AND TURPENTINES FROM RESINOUS WOODS.

1,264,551. Specification of Letters Patent. **Patented Apr. 30, 1918.**

Application filed September 10, 1912. Serial No. 718,546.

To all whom it may concern:

Be it known that I, David J. Ogilvy, a citizen of the United States, and a resident of the city of Cincinnati, in the county of Hamilton and State of Ohio, have invented certain new and useful Improvements in the Processes of Extracting Resins, Oleoresins, Oils, and Turpentines from Resinous Woods, of which the following is a specification, reference being had to the accompanying drawings, forming a part of this specification.

The usual solvent methods employed for the extraction and separation of the resins and oleoresins from resinous woods and such like are by the application with heat of such solvents, as petroleum distillates, pine oils, crude turpentine, alcohol, pine tar, rosin, and such like. I have discovered a more economical, safer from fire and explosion, and simpler method of procedure, the subject of the present invention; in which a resin solvent, water and heat are the agents, which will be more specifically pointed out and claimed.

In the drawing, the figure is a plan view in elevation of the apparatus used by me.

In operating this improved process, an apparatus is provided, having a digester or extractor 1, with ample openings for charging and discharging, each opening with its covers 2 and 3 respectively. This extractor 1 is practically filled with the resinous material to be operated on, as, for example, shreds, chips or sawdust from coniferous woods. A still 12 placed at a lower level than 1 is filled about three-fourths full of a mixture of the resin solvent and water. Heat is applied to the still 12 (by direct fire on the grate 4, if desired) and the liberated vapors of water and resin solvent are allowed to enter the extractor 1 preferably at the bottom through the pipe 5 which connects the still and the extractor. This pipe has valves 6 and 7, the valve 6 being opened and the valve 7 closed, when it is desired to have the combined vapors pass through the resinous wood. The result of the passing of these combined vapors through the resinous material is that the resins, oleoresins and turpentine oils present are washed out and carried back into the still 12 through the pipe 5, this operation being continued until the extraction is sufficient. A reflux condenser 8 is placed at a higher elevation than the extractor 1, so that the excess vapors of water, resin solvents and turpentines may be condensed and returned to the extractor 1 and the still 12. When the operation is completed, the still 12 containing the watery liquid and the resinous magma is connected with the exhaust condenser 9 and disconnected with the extractor 1, through the agency of the valves 6 and 7. The application of heat to the still 12 is continued and a preliminary separation of the resin solvents, turpentines and oils is made, the resulting distillate being further fractionated as desired. The resinous magma and watery liquor remaining in the still 12 are separated, and the magma utilized for the production of rosin products.

By inclosing the extractor 1 in brickwork as shown, the extractor may be then heated directly by furnace and flues 10, this modification being more convenient for treating the resinous woods and such like by submergence in the heated mixture of resin solvent and water. In this case, the resinous wood, preferably reduced so as to facilitate the action of the solvents, is introduced into the extractor 1, filling it about three fourths full, closing the valve 6 and the discharge cover 3. Enough of a mixture of resin solvent and water is added to just cover the resinous material under treatment. Heat is applied to the extractor 1 by the furnace and flues so long as there is evidence of sufficient resinous and oily material being extracted, the vapors from the operation being condensed and returned to the extractor 1 by the reflux condenser 8. When the extraction has been sufficient, the heating is discontinued and the watery liquor and resinous magma transferred to the still 12 by opening the valve 6. Any resinous magma remaining among the treated material may be removed by drenching with warm water. By now heating the resinous magma and the watery liquor in the still 12, opening the valve 7 and closing the valve 6 the resinous solvents and turpentine oils in vapor form

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pass into the exhaust condenser 9, and may have a preliminary separation, to be further fractionated as desired. The resinous magma remaining in the still 12 is separated from the watery liquor and is available for the production of rosin products.

Other designs of apparatus are available. The extractor and still may be combined in one vessel, extractors in which the resin solvents and water circulates. When the residual wood is required for pulp making an ordinary pulp digester with some alterations and additions may be utilized, thereby making the extraction of the resins and oils and the production of pulp all in one vessel.

When the resinous magma floats on the surface of the watery liquor, it may be easily removed by overflowing with water through pipe 11.

When the resinous wood operated on is rich in turpentines, it may be exposed to a preliminary steaming, and part of the turpentines will be carried over with the steam into the exhaust condenser 9. In this case, much of the resins are separated and remain mingled throughout the wood, and consequently are difficult to recover. By then adding a mixture of water and a resin solvent such as an .850 sp. gr. petroleum and heating the whole, the resins, oleoresins and turpentine oils will be assembled and at the same time more fully extracted from the wood, and may be then run off from the wood with the watery liquor, the chips being further drenched with hot water to remove more thoroughly any remaining resinous magma. When the resinous material operated on is practically free from turpentines such as resinous wood which has been exposed to the weather, or which has become impregnated with rosin such as cooperage, or batting dross and such like, the operation then becomes simplified in so far that the separation of the turpentine is not a primary object, and the resin solvents in such case may be used continuously until they become well saturated with turpentines and oils, it will then be time to fractionate and separate what turpentines and oils may be present.

The resin solvents required in my process depend on the final or ultimate use for which the resins are required; if in a hard and solid condition then it is proper to use a solvent which will evaporate easily in low pressure steam, whereas if the resin is required in a fluid or semisolid condition then a still heavier solvent should be used in the extraction as the solvent may become an integral part of the result. I prefer the refined distillates from mineral oils, coal tar and wood, which begin to boil at 120° C. (in absence of water) and distil dry about 220° C. Resin solvents which do not volatilize to any extent until the water begins to boil are preferable, as the resulting mixture of resin solvent vapor and steam is comparatively free from fire risk. Resin solvents which volatilize freely below 100° C., such as benzene, petroleum naphtha, wood and grain alcohol, are very effective in my process, provided the extra fire risk is no objection, while resin solvents which will not easily volatilize until exposed to high pressure or superheated steam are also very effective, such as petroleum oils, specific gravity .865 or .890. In using heavy resin solvents the separation of the turpentines and oils is simplified.

Among the advantages of this improvement are the following: economy in the quantity of resin solvent required, the facility of volatilizing and refluxing the resin solvents at a comparatively low temperature, reducing the tendency of the wood chips to pack. In the submergence method, the addition of salts such as calcium chlorid to the water, reduces the tendency of the wood chips to pack, and such salts are useful in increasing the temperature of the digestion and in vapor methods, resulting in quicker results.

Naphthalene is a desirable solvent in my process on account of its low price, its easy volatility, recovery and purification. Its specific gravity results in its being less buoyant in water than the lighter solvents, therefore it has a tendency to keep diffused more thoroughly among the wood chips in submergence.

The following few examples will illustrate proportions applicable in this improvement, taking an ordinary average grade of air dry pine wood in the form of chips.

For the vapor method:

Wood	30%.	Commercial xylene	20%.	Water	50%.
Wood	40%.	Petroleum S. G. .810	20%.	Water	40%.
Wood	50%.	Commercial benzol	10%.	Water	40%.
Wood	30%.	Alcohol	15%.	Water	55%.

For the submergence method, the following proportions give good results:

Wood	30%.	Naphthalene	20%.	Water	50%.
Wood	30%.	Petroleum S. G. .800 30%. Water	30%.	Calcium chlorid	10%.
Wood	15%.	Naphthalene	5%.	Water	80%.
Batting dross	25%.	Paraffin oil S. G. .890	25%.	Water	50%.

On account of the continuous presence of water or its vapor, and the comparatively low temperature at which the operation may be conducted, there is a minimum loss of the volatile contents.

The submergence method results in the uniform heating of the material.

In operating on sawdust by the submergence method, it is advisable to have a larger percentage of water present, than when chips are operated on, so as to prevent packing. In treating sawdust I prefer a refined petroleum sp. gr. .825, resulting in a resinous magma which floats, while the sawdust becoming saturated with water, sinks.

It will be noted that the waters and solvents are in each case applied in the same physical condition. The molecules of water and solvent, or of steam and vaporized solvent accompany each other and act simultaneously throughout the process. The efficacy of action and great fire protection in the extracting of rosins and turpentines from wood, is thus accomplished by me.

The matter of economy in the present process is a very important feature, the presence of the water or steam enabling me to divide and spread a small percentage of the solvent over a large surface, whereas if a same percentage of resin solvent was used minus the water it would practically be lost by being absorbed by the resinous wood operated on. Another advantage of my process is the low temperature at which the operation may be conducted, the presence of the water enabling the resin solvent to volatilize at a lower temperature than when the resin solvent is volatilized alone; as for example, wood 15%, naphthalene 5%, water 80%. Such a mixture operates satisfactorily at the temperature of the boiling water. Now omit the water and try the extraction of the resins from the wood with naphthalene alone, which volatilizes very slowly until it arrives at its boiling point, viz.; 218 C.; whereas when water is present the naphthalene volatilizes quite freely at the temperature of the boiling water. In the case where alcohol is used as the agent, when the dilute alcohol is introduced into the still, the mixed vapors which pass into the resinous material usually have a preponderance of alcohol, thus rendering it more active as a solvent; this solution returning to the still, is revolatilized leaving the resins remaining in the still and the alcohol passing up with the steam among the resinous wood continues the action.

Taking all in all, then, among the advantages of this improvement are the following: The operation may be conducted at a comparatively low temperature. The continual presence of water or its vapor reduces the risk of fire and explosion. The water and steam assist in disintegrating the wood so that the resin solvents may have free action. The presence of the water or steam divides and spreads the resin solvent, even when a minimum percentage of resin solvent is used. It facilitates the refluxing or returning of the resin solvent to the extractor or the still, so that it may be revaporized and continue its action on the resinous wood.

The use of water in either liquid or vapor form at substantially the boiling point of water, being so closely allied, the chemical term H_2O seems applicable in a broad sense to express the essence of my invention, and it is so used in the claims, when either steam and water or both is intended. Thus a reservoir filled full of wood and only part full of water and solvent, would use both the water and the steam process.

I claim:

1. The method of extracting and separating the resins, oleoresins, oils and turpentines from resinous woods and the like, which consists in submerging the resinous wood to be operated on in a mixture of water and resin solvent, and exposing the whole to heat to boil the mixture, substantially as described.

2. The method of extracting and separating the resins, oleoresins, oils and turpentines from resinous woods and the like, which consists in exposing the wood to an initial heating in water, adding resin solvents, then continuing the heating at the temperature required to boil the water in presence of the resin solvent and wood.

3. The method of extracting and separating the resins, oleoresins, oils and turpentines from resinous woods, which consists in exposing a mixture of comminuted resinous wood, a resin solvent and water at the temperature necessary for boiling in the mixture, to active circulation and agitation so as to retard the settling and cohering of the comminuted wood.

4. The method of extracting and separating the resins, oleoresins, oils and turpentines from resinous woods and the like, which comprises exposing the wood to the combined action of resin solvent and water at the temperature necessary to boil same in conjunction with a resin solvent, then exposing the resulting resinous magma to a further heating so as to separate the light oils and turpentines from the resinous magma by distillation.

5. The method of extracting and separating the resins, oleoresins, oils and turpentines from resinous woods, which comprises the subjection of a proportion of wood to the combined action of a mixture of water and a resin solvent at the temperature necessary to boil same in the mixture in pro-

portions larger and smaller than the proportions of wood respectively.

6. The method of extracting and separating the resins, oleoresins, oils and turpentines from resinous woods, which consists in exposing the wood to the action of water at the temperature necessary to boil same in conjunction with an oily and spirituous resin solvent, resulting in the resinous and oily constituents of the wood being separated in the condition of a magma, then exposing said magma to heat in a still to remove the lighter turpentines and oils, leaving the heavier oily constituents in combination with the resins.

7. The method of extracting and separating the resins, oleoresins, oils and turpentines from resinous woods, which consists in treating the woods simultaneously with resin solvents and H_2O at a temperature substantially that of the boiling point thereof.

8. The method of extracting and separating the light oils and turpentines from resinous woods and the like, which comprises the subjection of the resinous woods to the action of resin solvents in the presence of H_2O at boiling temperature.

9. In the extraction of rosin and turpentine from coniferous wood, the process which comprises simultaneously treating such wood in a comminuted state with water and a volatile solvent at their joint boiling point till the rosin and oils are dissolved and extracted by such volatile solvent, the amount of such volatile solvent present being greater than that naturally present in the wood.

10. In the extraction of rosin and turpentine from coniferous wood, the process which comprises heating such wood at a temperature below 100° C. in the presence of water vapor and vapors of a volatile solvent till the rosin and oils are extracted by such volatile solvent, the amount of volatile solvent present being greater than that normally existing in the wood.

DAVID J. OGILVY

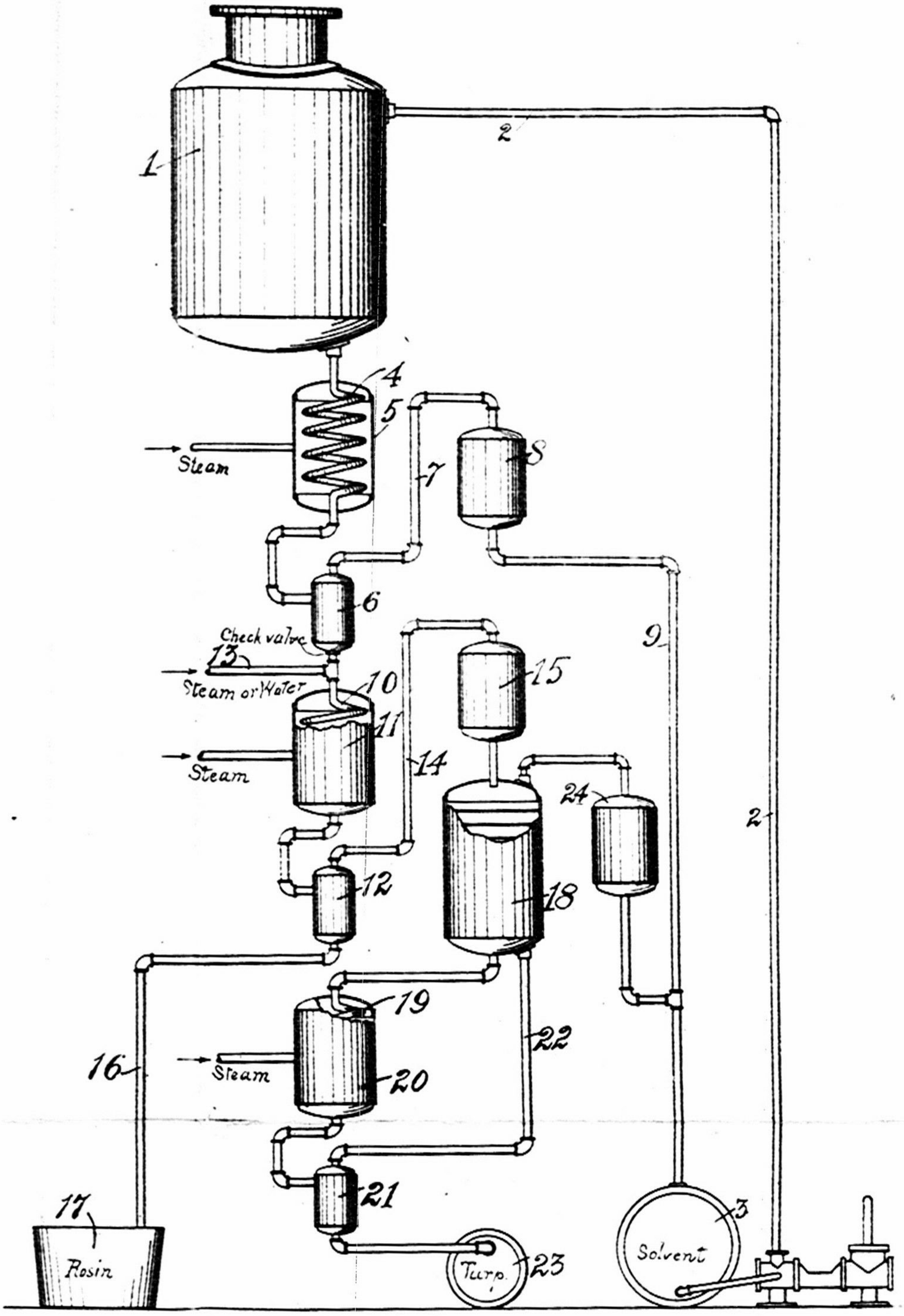
Witnesses:
MARTIN ALLEN,
K. SMITH.

H. T. YARYAN.

PROCESS FOR REMOVING TURPENTINE AND ROSIN FROM RESINOUS WOODS.

APPLICATION FILED AUG. 31, 1908.

915,400. Patented Mar. 16, 1909.



Witnesses:

M C Cowley

Ada E. Cameron

Inventor:

By Homer T. Yaryan

By [illegible] Hall Atty.

UNITED STATES PATENT OFFICE.

HOMER T. YARYAN, OF TOLEDO, OHIO.

PROCESS FOR REMOVING TURPENTINE AND ROSIN FROM RESINOUS WOODS.

No. 915,400. Specification of Letters Patent. Patented March 16, 1909.

Application filed August 31, 1908. Serial No. 451,013.

To all whom it may concern:

Be it known that I, HOMER T. YARYAN, a citizen of the United States, residing at Toledo, in the county of Lucas and State of Ohio, have invented certain new and useful Improvements in Processes for Removing Turpentine and Rosin from Resinous Woods; and I do declare the following to be a full, clear, and exact description of the invention, such as will enable others skilled in the art to which it appertains to make and use the same, reference being had to the accompanying drawings, and to the figures of reference marked thereon, which form a part of this specification.

In the process of extracting turpentine and rosin from resinous woods by means of a hydrocarbon solvent,—such as naphtha,—the recovery of the rosin from the solution, by distillation, is a comparatively simple matter, but the complete separation of all the turpentine from the solution presents difficulties which have heretofore prevented the adoption of such process on a commercial scale. This difficulty is due to the fact that in vaporizing and distilling a mixture of two or more volatile liquids having different boiling points, the lighter or more volatile vapors will carry over the heavier in increasing proportions as the boiling solution approaches the point of the complete separation of the lighter constituents. This renders necessary the further and repeated fractionation of the distillate, and as heretofore practiced, involves such expense and outlay of time and labor as to preclude the profitable use of the hydrocarbon process.

My invention is designed to overcome the difficulties here indicated, and to provide a process by means of which all the turpentine and rosin may be extracted from resinous woods, and by means of which the turpentine and rosin and solvent may be rapidly and economically separated and recovered.

I practice my process by means of the apparatus shown diagrammatically, by way of illustration, in the single figure of the accompanying drawing.

The process may most conveniently be described and understood by explaining the apparatus and its operation, which is as follows: The resinous wood to be treated is, in comminuted form, placed in the closed chamber of a stout iron tank or extractor 1. The wood is liberally sprayed or bathed with benzin, naphtha, petroleum or other suitable hydrocarbon introduced through pipe 2 from the hydrocarbon tank 3. The bath of hydrocarbon penetrates the woody particles and dissolves and washes out from the chips the turpentine and rosin. From the bottom of the extractor the solution is conducted through a coil 4 inclosed in a steam drum 5, which coil discharges into a separating chamber 6. The steam around the coil 4 is at such pressure and temperature as to heat the liquid flowing through the coil sufficiently to vaporize the hydrocarbon solvent, but not the turpentine,—say 240° F. When the liquid flows into the separating chamber 6, the liberated vapor escapes through pipe 7 into condenser 8 from whence it flows through pipe 9 back to the hydrocarbon tank 3 to be again used.

The unvaporized contents of the separating chamber 6 are conveyed through a second heating coil 10, inclosed in a steam drum 11, to a second separating chamber 12. The liquid in its course from the first separating chamber to the second is mixed with steam or water through pipe 13 to facilitate the vaporization of the turpentine and solvent. The steam in and surrounding the coil 10 is of such pressure and temperature,—say 280° F.,—as to vaporize the turpentine and solvent flowing therethrough. When the liquid from the coil 10 is discharged into the separating chamber 12 the liberated vapor flows through pipe 14 to condenser 15 leaving the rosin to be trapped off and condensed through pipe 16 to its receptacle 17.

Owing to the law governing the vaporizing of a mixture of two or more volatile liquids, above indicated, the turpentine has now carried with it from the separating chambers 6—12 to the condenser 15 a considerable percentage of the solvent. To effect the separation of this turpentine and solvent the solution is conducted from the condenser 15 into and through a rectifying column 18, of the usual or any preferred construction. The liquid flowing from the rectifying column is conducted through a heating coil 19 in steam drum 20 from whence the liquid is conducted to a third separating chamber 21. The steam surrounding the coil 19 is of such pressure and heat as to raise the temperature of the liquid flowing through the coil to, say, 306° or just below the boiling point of turpentine. When the liquid from the coil

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19 is discharged into the separating chamber 21 the liberated vapor, principally solvent with some turpentine, passes through pipe 22 to the bottom of the chamber of the rectifying column while the unvaporized liquid,—turpentine,—is trapped off to the turpentine tank 23. The drip from the condenser 15 through the perforated floors of the column 18 is met at each floor by the ascending vapors from the separating chamber 21 and thus the ascending vapors have their heavier portions condensed while the more volatile vapors of the solvent continue to ascend. The dripping solution also has a portion of its solvent expelled in the form of vapor which ascends with the vapor coming from below, passing finally into condenser 24 from whence the solvent, now freed from its turpentine, passes to the tank 3. The dripping solution from which the solvent is thus rectified continues on through the coil 19 and separating chamber 21 to tank 23 giving up in its course, as vapor, the constituents having a lower boiling point than that fixed for the turpentine, these vapors being returned to the column 18 to be treated in turn as above described. Thus, it will be seen, the rosin, turpentine and solvent are completely separated and conveyed to their respective receptacles.

In the accompanying graphic illustration of my apparatus I have not shown the details of minor parts, such as valves, traps, dash-plates, pumps, and the like, as these will be understood by those skilled in the art, without further illustration. It will also be understood without illustration that a series of extractors may, if desired, be employed in connection with the remainder of the apparatus above described, in such manner that the process shall be practically continuous. It is also obvious that, if desired the vaporization of the solutions may facilitated by placing the liquids under a partial vacuum by means which are well understood.

Having described my invention, what I claim and desire to secure by Letters Patent is,—

1. The process of removing turpentine and rosin from resinous woods which consists, first, in treating the wood with a hydrocarbon solvent whereby the turpentine and rosin are removed in solution; second, by distilling from this solution the greater part of the solvent and then the turpentine with the remaining solvent, whereby the rosin is recovered, and, third, by passing the mixture of turpentine and solvent through a rectifying column, to separate and recover the turpentine and solvent.

2. The process of removing turpentine and rosin from resinous woods which consists in treating the woods with volatile hydrocarbon solvent, then passing the solution through a coiled evaporator to remove the greater portion of the solvent, then passing the remaining solution through a second coiled evaporator with steam by which the turpentine and the remainder of the solvent are removed and the rosin is recovered, and finally passing both the remaining solvent and turpentine through a rectifying column whereby the turpentine and solvent are separated and recovered.

3. The process of removing turpentine and rosin from resinous woods which consists in treating the woods with a volatile hydrocarbon solvent, then distilling the solution thus obtained to recover the greater portion of the solvent, then distilling the remainder of the solution to separate and recover the rosin, then passing the remaining solution through a rectifying column, then distilling the liquid discharged from the rectifying column to recover the turpentine, then returning the vapors from the last mentioned distillation to the rectifying column, and then conducting the uncondensed portion of said vapors to a condenser to recover the solvent.

4. The process of removing turpentine and rosin from resinous woods which consists in treating the woods with a volatile hydrocarbon solvent, then passing the solution thus obtained through a heating coil into a separating chamber, then conducting the liberated vapors from such separating chamber through a condenser to a receptacle for the solvent, then conducting the remaining solution through a heating coil into a second separating chamber, then conducting the liberated vapors from said second separating chamber to a second condenser to separate and recover the rosin, then conducting the remaining solution from said second condenser through a rectifying column and through a third heating coil into a third separating chamber, then removing the unvaporized liquid from said third separating chamber whereby the turpentine is recovered, then conveying the liberated vapors from said third separating chamber back to the rectifying column, and then conveying the uncondensed vapors from the rectifying column to a condenser, whereby the remaining solvent is recovered.

5. The process of removing turpentine and rosin from resinous woods which consists in treating the woods with a volatile hydrocarbon solvent, then passing the solution thus obtained through a heating coil into a separating chamber, then conducting the liberated vapors from such separating chamber through a condenser to a receptacle for the solvent, then conducting the remaining solution mingled with added steam through a heating coil into a second separating chamber, then conducting the liberated vapors from said second separating chamber to a second condenser to separate and recover the rosin, then conducting the remaining solution from

said second condenser through a rectifying column and through a third heating coil into a third separating chamber, then removing the unvaporized liquid from said third separating chamber whereby the turpentine is recovered, then conveying the liberated vapors from said third separating chamber back to the rectifying column, and then conveying the uncondensed vapors from the rectifying column to a condenser, whereby the remaining solvent is recovered.

In testimony whereof I affix my signature in presence of two witnesses.

HOMER T. YARYAN.

Witnesses:
CLAYTON MURPHY,
ADA E. CAMERON.

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T. W. WRIGHT.

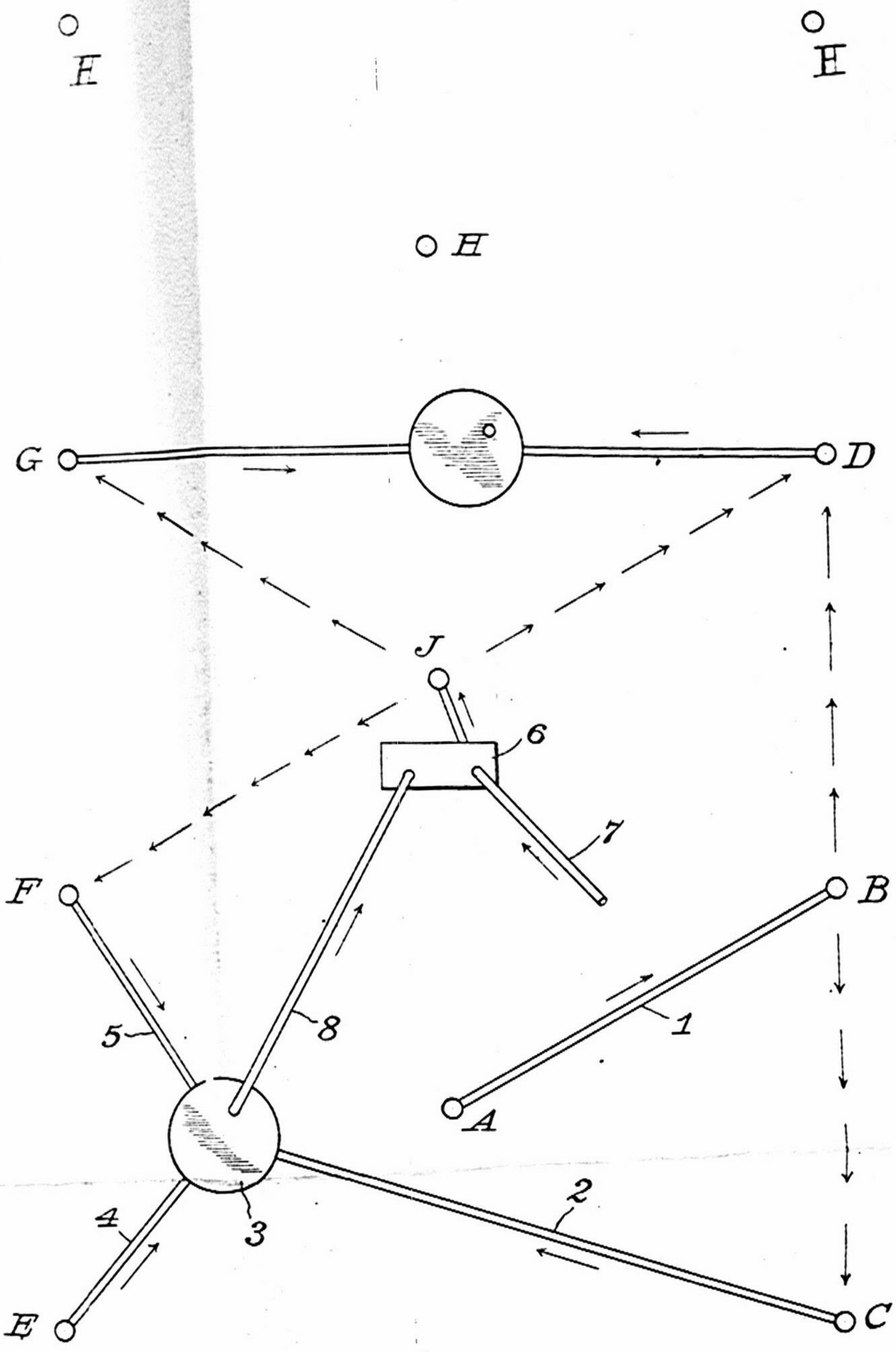
METHOD FOR CONSERVING NATURAL GAS AND OIL.

APPLICATION FILED DEC. 20, 1912.

1,101,605. **Patented June 30, 1914.**

2 SHEETS—SHEET 1.

Fig. 1



WITNESSES:

L. J. Fischer

K. Imboden

INVENTOR:

Thomas W. Wright

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ATTORNEY

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117

T. W. WRIGHT.

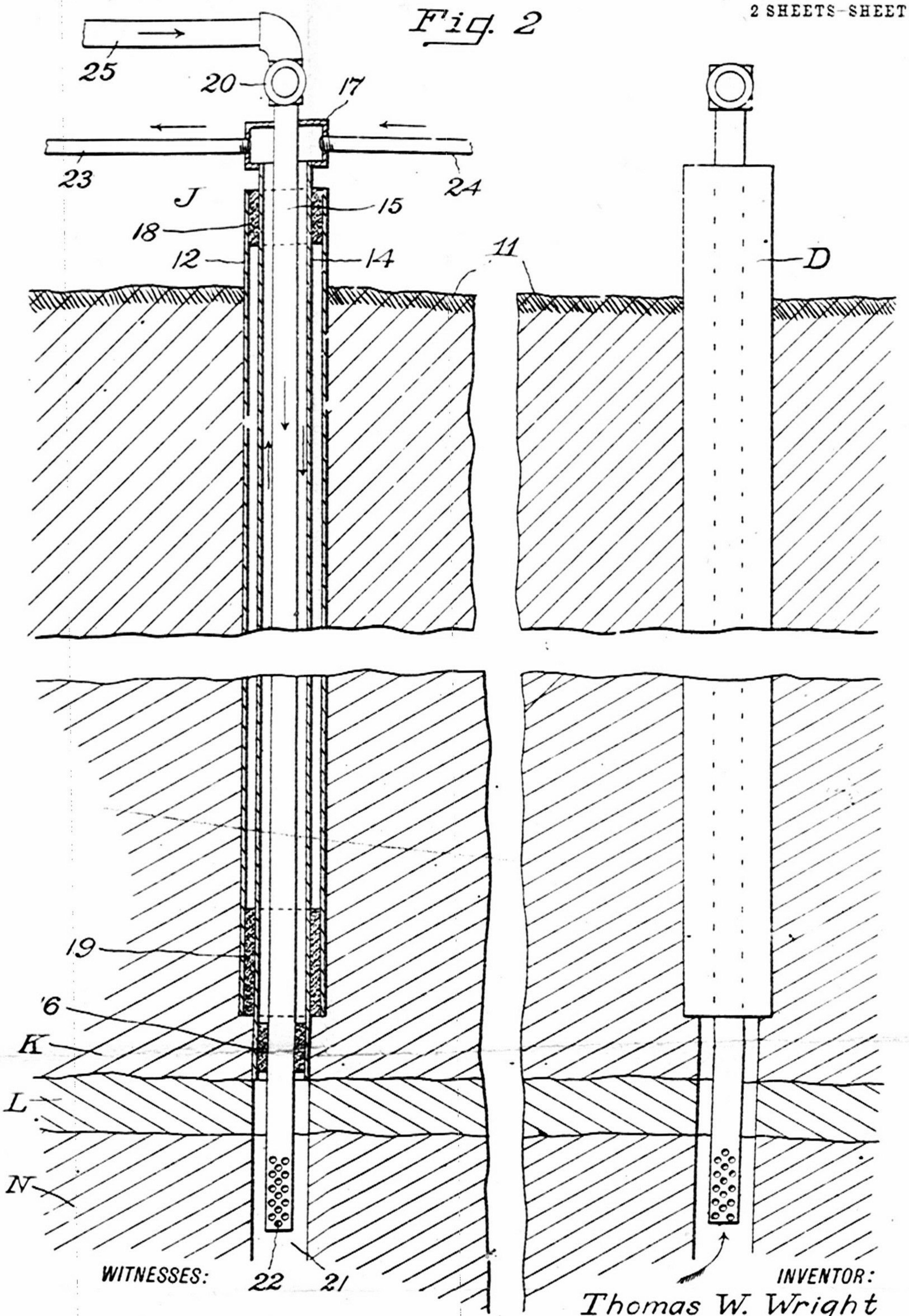
METHOD FOR CONSERVING NATURAL GAS AND OIL.

APPLICATION FILED DEC. 20, 1912.

1,101,605. Patented June 30, 1914.

2 SHEETS—SHEET 2.

Fig. 2



WITNESSES:

L. J. Fischer

K. Imboden

INVENTOR:

Thomas W. Wright

BY F. G. Fischer

ATTORNEY

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Line 35-40

UNITED STATES PATENT OFFICE.

THOMAS W. WRIGHT, OF HENRYETTA, OKLAHOMA.

METHOD FOR CONSERVING NATURAL GAS AND OIL.

1,101,605. Specification of Letters Patent. Patented June 30, 1914.

Application filed December 20, 1912. Serial No. 737,871.

To all whom it may concern:

Be it known that I, Thomas W. Wright, a citizen of the United States, residing at Henryetta, in the county of Okmulgee and State of Oklahoma, have invented certain new and useful Improvements in Methods for Conserving Natural Gas and Oil, of which the following is a specification.

My invention relates to a method of conserving natural gas and using the gas for the extraction of petroleum from fields where the oil could not otherwise be brought to the surface except by pumping.

Millions of feet of natural gas waste into the atmosphere every day in some districts owing to lack of artificial reservoirs for same.

One object of my invention is to save this gas, and not only this, but to employ it as a medium for the extraction and enrichment of oil which is forced to the surface by the pressure thereof.

The gas which I refer to above as going to waste, rises in some wells from the oil contained in the oil-bearing rock. In other wells in the same vicinity, the gas may have ceased to issue, though the oil deposits therein may be as great as in the other instance. The pressure of the wasting gas issuing from some wells is very great. The main idea of my invention is to divert and conserve such gas by turning it into a non-gas-producing, but oil containing well, shutting in said well to prevent the escape of gas and oil therefrom; taking the gasolene-charged oil from other (now dead) wells in the same field; storing the oil in tanks having closed tops; and recovering the gas from the space above the oil in such tanks. One million feet of gas can be stored under pressure in the space of 50 to 100 barrels of petroleum. In practice, I may employ natural gas from a well at a pressure insufficient to raise oil in adjacent wells, but by means of a compressor raise the pressure to a sufficient point for that purpose.

Among other advantages which I claim are: The oil can be drained from the beds in less time than under the present system. A larger production and a cheaper method of extracting the oil. Utilizing subterranean spaces for the storage of gas.

In order that my invention may be fully understood, reference will now be made to the accompanying drawings, in which:

Figure 1 is a plan view of a group of eleven wells, showing apparatus that may be employed in the practice of my invention. Fig. 2 is a diagrammatic view in vertical section of two not far distant wells, one of which is equipped with means for practising my invention. On Fig. 1, the small circles represent wells of the usual kind.

A designates a well from which gas issues at a pressure sufficiently high for my purpose without requiring pumping or compression.

B designates a well which taps oil-bearing rock but has ceased to yield oil by natural pressure. I connect the casing of well A to an inner tube of well B by a suitable pipe 1. The gas in well B becomes liquefied by the high pressure and by cooling means (presently described), and the gasolene thus formed permeates the oil-bearing rock and drives the oil therefrom to other parts of the field, which are tapped by other wells as C, D, E, F, G, H, J. The aforesaid pressure now causes oil to rise through one or more of said wells, say through well C. From this well, I run a pipe 2 to the lower part of a closed-top steel storage tank 3, of large capacity for both oil and gas. From this reservoir, oil and gas may be taken and sold when good markets exist. Other wells, as E and F, that may yield oil under my invention, may be connected to the same reservoir 3, as by pipes 4, 5.

6 designates a shed containing a gas compressing pump. Gas from any source, may be taken to said pump by a pipe 7, and compressed for use as aforesaid in an adjacent well J. Of course the gas might be drawn from the reservoir 3, as indicated by pipe 8.

It is to be understood that none of the wells on the group shown, may yield gas for my purpose. In that case, gas may be piped from a well at any point which is not excessively distant and brought to the local oil field, the cost of piping and labor being the only limitations on such transportation. The producing well A is shown here merely for convenience of illustration.

The simplest method in which I contemplate preparing a receiving well as J, is shown in Fig. 2, in which: 11 designates the land surface: K, a cap rock stratum at the bottom of the wells J and D, which may be as much as a mile or more apart. L and N

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Growth of Industry.—The making of gasoline from natural gas increased from a production of a few thousand gallons in 1904 to about 43,000,000 gal. in 1914. Not until 1909 did the industry assume commercial importance. According to the United States Geological Survey, the increase in production of gasoline for the year 1912 over 1911 was 63 per cent.[1] The rate of increase for the year 1913 over 1912 was 100 per cent. The gas used represents that which previous to the installation of plants for the production of gasoline was principally wasted, being, for the most part, "wet" gas which comes from the casing heads of oil wells.

Constituents of Natural Gas—Natural gases are mixtures in which the hydrocarbons of the paraffin series predominate, and methane is the preponderating constituent, the characteristic hydrocarbon of all natural gases. Small quantities of nitrogen, carbon dioxide, and water vapor constitute the impurities. In some gases, however, the percentages of nitrogen and carbon dioxide are large. One analysis has been published in which nitrogen comprised 98.5 per cent. of the total, and another in which the carbon dioxide equaled about 30 per cent. of the total.

The exact proportions of the constituents in natural gases cannot be determined by ordinary methods of analysis, although the total quantity of paraffin hydrocarbons can be thus obtained and the heating value and specific gravity determined. Natural gas may be separated into its constituents by liquefying it by means of liquid air and separating the constituents of the liquefied gas by fractional distillation. By this means Burrell, Seibert and Oberfell[2] showed that the natural gas used in Pittsburgh contained 84.7 per cent. methane, and that an extremely "wet" gas from which gasoline is condensed commercially contained only 36.8 per cent. methane.

The paraffin hydrocarbons that principally concern the gasoline producer are methane, ethane, propane, and the butanes, pentanes, hexanes, and heptanes. Of these, the first four are gases at ordinary temperatures, the last three liquids. The gases after contact with the oil in the earth bring with them the vapors of the liquid hydrocarbons. The vapors are carried along with the permanent gases in the same manner that water

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[1] On the production and technology of the natural-gas gasoline industry in 1912, see *Oil, Paint and Drug Rept.*, 85 (1914), No. 13, p. 33.

[2] *Bull.* 88 of the *United States Bureau of Mines.*

TABLE XLI.—ANALYSES OF NATURAL GASES FROM VARIOUS FIELDS[1]

	Constituents								Remarks	Analyst
	Methane	Carbon monoxide	Carbon dioxide	Nitrogen	Oxygen	Hydrogen	Other hydrocarbons	Other constituents		
California—Fresno County, Coalinga Field	88.00		11.10	0.90					Collected by G. H. Salisbury, June 10, 1910.	G. A. Burr
King County, Sunset Field	87.70		10.50	1.80					Collected by I. C. Allen, July 16, 1909.	G. A. Burrell.
Los Angeles County, West Los Angeles	91.00		1.00	5.20	0.10		2.70		Collected by I. C. Allen, July 23, 1909.	G. A. Burrell.
Santa Barbara Co., Santa Maria Field	62.70		15.50	1.40	0.20		20.20		Collected by I. C. Allen, Aug. 5, 1909.	G. A. Burrell.
Kansas—Allen County, Iola	94.50			5.08	0.23			H-trace He-0.18	Collected June 10, 1906	Hamilton P. Cady and David F. McFarland.
Chase County, Elmdale	78.60		0.15	12.13	0.30		8.26	He-0.56	Depth, 152 ft.; pressure, 45 lb.; collected Oct. 6, 1906.	Hamilton P. Cady and David F. McFarland.
Louisiana—Caddo field	95.00		2.34	2.56				0.01		F. C. Phillips.
New York—Chautauqua Co., Fredonia	90.05		0.41	9.54						F. C. Phillips.
Pennsylvania—McKean County, Kane	90.38		0.21	9.41	Tr.					F. C. Phillips.
Washington County, Houston	84.26		0.44	15.30	Tr.				Contains also trace of ammonia.	F. C. Phillips.
Westmoreland Co., Murrysville	97.70		0.28	2.02	Tr.					F. C. Phillips.
West Virginia—Marion County, Fairmont	81.60	0.40	0.10	3.21	0.20	0.20	14.29			C. C. Howard.
Austria—Wels	97.10		1.30	1.00	0.60				Specific gravity (air = 1), 0.5667.	
Germany—Neuengamme near Hamburg	91.50		0.30	4.60	1.50		2.10			
Hungary	92.05		0.65	7.30						
Russia—Samara	53.35		1.17	40.86	4.22		0.40			
Daghestan	65.84		12.82					Ethane, 19.92		
Tchelcken	77.30	3.50	3.60	8.90	1.80			Olefines, 4.80		
Caspian Region	93.07		2.18	0.49		0.98		Olefines, 3.26		
Baku (Peninsula of Apscheron)	92.89		0.93	2.13		0.34		Olefines, 4.11		
England—Staffordshire, Charlemont	99.60		0.30	0.10						
Sussex, Heathfield	93.16	1.00		2.90				Ethane, 2.94		

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[1] For additional analyses, see CLARKE's "Data of Geochemistry," *Bull.* 616, *U. S. Geol. Survey*, 715; and *Bull.* 88 of the *Bureau of Mines*, 21 and 22. For a comparison of the composition of natural gases throughout the world, see NIEDERSTADT, *Z. öffent. Chem.*, 20 (1914), 386. On the occurrence of natural gas, see HAGER, *Eng. Min. J.*, 100 (1915), 959.

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vapor exists with air. After treatment in the gasoline plant, where the capacity of the gases to carry the vapors is much lessened, the vapors are deposited.

Factors Affecting Yield of Gasoline from Natural Gas.[1]—The quantity of gasoline vapors in any particular gas mixture is dependent upon the character of the oil in the sand, the temperature and pressure existing in the sands, the porosity or closeness of the strata, the intimateness of contact between gas and oil, and other less important factors. The pentanes, hexanes, and heptanes are the only constituents of crude oil that, at earth temperatures, have vapor pressures of such magnitude that they are distilled in quantity from the crude oil; hence, they are the chief liquid constituents of natural-gas gasoline.

In wells yielding gas suitable for gasoline condensation, the three gases, methane, ethane, and propane, invariably occur in the gaseous condition, and butane also is usually present in the gaseous condition.

Methods of Testing for Gasoline Yield.—By itself the ordinary eudiometric analysis is of little use for testing a sample of natural gas in order to determine its suitability for gasoline production. Laboratory methods in principal use have to do with solubility and specific gravity tests. The Bureau of Mines has used alcohol and claroline oil; 100 c.c. of the gas is shaken with 35 c.c. of the oil or with 50 c.c. of the alcohol until absorption ceases. For the determination of specific gravity Burrell and his co-workers have both weighed the gas and used Bunsen's effusion method. These investigators have found that natural gases at present used for gasoline production have a specific gravity of 0.80 or higher, and are soluble to the extent of 30 per cent. or more in the solvents used. Laboratory tests serve best as preliminary indications previous to tests of the gas at the well by means of an experimental compressing plant.

Use of Pitot Tube and Gas-Analysis Apparatus.—The Pitot tube as ordinarily used for measuring the flow of gases, that is, where the static pressure is not obtained, may give results that are 8 per cent. in error, even though the tube is correctly used. When the static pressure is obtained and all readings are taken with a sufficient degree of refinement, they may vary only 1 per

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[1] Burrell, Seibert and Oberfell, *loc. cit.* It may be noted that by absorption methods much of the so-called "dry" natural gas can be treated.

FOR MR. JUSTICE VAN ORSDEL

COURT OF APPEALS
DISTRICT OF COLUMBIA
FILED

JAN- 9 1933

Henry W. Hodges
CLERK

Court of Appeals, District of Columbia

April Term, 1932

No. 5762

Henry L. Doherty, *Appellant*,

vs.

Thomas E. Robertson, Commissioner of Patents,
Appellee.

Appeal From the Supreme Court of the District of Columbia.

BRIEF ON BEHALF OF APPELLANT.

Edmund G. Borden,
Attorney for Appellant.
J. Austin Stone,
Of Counsel.

Kenneth I. White,
Of Counsel.

Press of Byron S. Adams, Washington, D. C.

Court of Appeals, District of Columbia

APRIL TERM, 1932

No. 5762

HENRY L. DOHERTY, *Appellant*,

vs.

THOMAS E. ROBERTSON, Commissioner of Patents,
Appellee.

Appeal From the Supreme Court of the District of Columbia.

BRIEF ON BEHALF OF APPELLANT.

Appellant, Henry L. Doherty, appeals from a decree of the District of Columbia Supreme Court dismissing his Bill in Equity filed under U. S. Revised Statutes Section 4915. Appellant's Bill (Rec. p. 1), prays for an order directing Appellee, Commissioner of Patents, to grant him U. S. Letters Patent on the invention described in his patent application, S. N. 167,865, filed in the Patent Office February 12th, 1927, and for such other and further relief as may be just and proper.

The primary question at issue is whether Appellant's patent application (Rec. pp. 38-42) describes and claims a patentable invention in view of the disclosure of U. S. Patent to Wright No. 1,101,605, dated June 30, 1914 (Rec. pp. 116-119). To correctly answer this question, it is necessary to first consider and properly determine certain questions of fact.

The decree of the Supreme Court (Rec. p. 9) adopts certain Findings of Fact and Conclusions of Law (Rec. p. 8), submitted by Appellee, without written opinion. The principal error assigned to the decree is in its failure to take cognizance of certain additional questions of fact, which, if properly determined should, in Appellant's opinion, result in a finding in Appellant's favor on the primary question of law, and a reversal of the decree.

At the trial of the case on February 25, 1932, before Mr. Justice O'Donoghue, Charles T. Beecher of Bartlesville, Oklahoma, was called as a witness on behalf of Appellant. Mr. Beecher's testimony was taken as that of an experienced petroleum production engineer, for the purpose of rebutting conclusions of the Patent Examiner which were deemed by Appellant to be erroneous, but which conclusions were accepted by Appellee as those of "an expert in this art" in his denial of Appellant's application for patent. Mr. Beecher is well known to the petroleum industry as an experienced petroleum engineer. He has served as national chairman of the Technical Division of the American Petroleum Institute, and during the past year as national chairman of the Petroleum Division of the American Institute of Mining and Metallurgical Engineers. Mr. Beecher's testimony is outlined in the Statement of Evidence (Rec. pp. 16-36) while the Conclusions of the Patent Examiner appear in his Statement (Rec. pp. 43-47). Appellee's refusal of Appellant's application for patent is expressed in the decision of the Patent Office Board of Appeals (Rec. pp. 47-49).

Comparison of Doherty Application and Wright Patent Disclosure.

Both the Doherty application and the Wright patent are concerned with the problem of increasing the recovery of petroleum from oil bearing sands usually located thousands of feet below the earth's surface, through wells. Present methods of production recover only a small fraction, average 20 to 25 per cent, of the oil present in such sands. The difficulties of the problem, and the factors adversely affecting increased recovery of oil by production methods now in use, are discussed in Uren's article (Exhibits D and E) (Rec. pp. 50-57) to which attention is respectfully directed. Physical samples of oil sand are in evidence as Plaintiff's Exhibit "C" (Rec. pp. 20, 21).

The Wright patent issued in 1914, and has not contributed materially to solution of the problem (Rec. p. 30). The Doherty application describes and claims what is considered to be a distinctly practicable and patentable improvement over the method of recovering petroleum which is disclosed by the Wright patent.

Both Doherty and Wright propose to increase the recovery of petroleum from a deeply buried oil-bearing sand by introducing a volatile hydrocarbon substance under pressure to the oil sand. Wright was not the first to suggest that a greater recovery of oil could be had by introducing natural gas under pressure into the oil sand (Rec. p. 35 and file references of Wright Patent—Exhibit B). Doherty's process is distinguished from that of Wright, and Wright's process was held by the Patent Office to distinguish from prior practice, chiefly in the character of the hydrocarbon substance employed as a medium for increasing or boosting the recovery or flow of petroleum from buried oil sands through wells.

Long prior to Wright, it was old to introduce natural gas under pressure to an oil sand through a gas injection well penetrating the sand, for the purpose of building up gas pressure in the sand to thereby *drive* increased volumes of petroleum ahead of the built up gas pressure toward an oil recovery well. The gas thus introduced did not go into solution in the oil to any extent, because, as explained by Lacy (Rec. p. 83—Fig. 15), it takes about 9-35 years to **half** saturate by diffusion a stationary body of oil ten feet deep with methane gas under pressure contacted with the surface of the oil (Rec. p. 25).

Wright's Invention.

Wright's contribution to the art, if any, was to propose means for liquefying "gasolene" components of the injected hot natural gas, and to introduce the liquid "gasolene" into **solution** in the oil to thereby "**thin**" the oil. The pertinent portions of the Wright patent describing his process are embodied in the Record at page 118, lines 29-33, and 65-81, and page 119, lines 3-42.

Wright's patent process can only be correctly interpreted as introducing to the underground oil stratum a flow-inducing medium having two components, namely **unliquefied gaseous** hydrocarbons and **liquefied "gasolene"** hydrocarbons. Wright has **erroneously** designated his liquefied "**gasolene**" as "liquefied **gas**" in certain parts of his patent, and **this has apparently misled both the Court and Appellee.** Natural gas "gasolene" is composed chiefly of hydrocarbons which are **liquid** at normal temperature and pressure (Rec. p. 122—Defendant's Exhibit 2). If Wright's "gasolene" were really a liquefied gas, it would not be present as a liquid in admixture with the oil removed through the wells "D", as described by Wright (Rec. p. 119, line 40), but would have escaped from solution in the oil as the oil approached the zone of high temperature and low, substantially atmospheric, pressure existing at the bottom inlet of the well "D" (Rec. pp. 22, 23).

According to Wright, the **natural gas entering** the top of well J is **hot** (Rec. p. 119, line 29). Wright proposes to cool the gas flowing down the tubing 15 to the oil sand by thermal circulation of brine in the annular chamber lying between tubing 15 and tubing 14 (Rec. p. 119, lines 31-35). This chamber may be say 2000 feet long and 6 inches outside diameter, 2 inches inside diameter (Rec. p. 27). The brine enters through pipe 24 and exits through pipe 23.

The system of gas cooling by thermal circulation of brine proposed by Wright is practically inoperative, as explained by witness Beecher (Rec. pp. 26-28). Particularly is Wright's proposed gas cooling system impractical and inoperative for liquefying gaseous hydrocarbon components of natural gas such as propane and butane. Propane liquefies at —40° F. Butane liquefies at 26° F. Gas enters the top of Wright's well J probably at a temperature above 100° F. (Rec. p.

119, line 29). Cold brine entering Wright's proposed cooling system through pipe 24 will pass right on through the top section of pipe 17 and out through pipe 23, without any substantial circulation. The modification of the Wright patent cooling system proposed by the Court (Rec. p. 27) is unwarranted by Wright's disclosure, and would not be practical as explained by Witness Beecher (Rec. pp. 27, 28). It should be apparent that it is impossible to get thermal circulation of brine in a chamber of great height and small cross section such as Wright relies on to cool his injected gases. Even if it were possible to secure thermal circulation of brine about tube 15 of Wright throughout its length, for example 2000 feet, it would not be possible or practical to liquefy any gaseous components of the gas in this manner because of the high degree of cooling which would be required to effect liquefaction of even any butane content of the gas during the relatively short time which each unit volume of the gas takes to pass through the length of the inlet tube in a commercially practical oil sand repressuring operation.

Doherty's Improvement.

Doherty's flow boosting medium is **liquefied propane-butane** saturated with methane and ethane. There is no disclosure of this type of reagent in the Wright patent. The Court and Appellee have **erroneously assumed** that Wright's brine cooling system would be operative not only to liquefy any propane-butane present in the gas, but also to effect saturation of any propane-butane, thus liquefied, with methane and ethane.

Practical application of the Doherty process requires that the **propane and butane be liquefied** by very efficient refrigeration **before being introduced to the in-**

jection well. Likewise **saturation of the liquid propane-butane with methane-ethane gas must be completed** by intimate contact of the gas and liquid, as by bubbling the gas through the liquid under high pressure and accompanied by refrigeration, **before the gas enters the well,** so that the flow-boosting medium remains in liquid state at the time it reaches the underground oil body where the temperatures are considerably higher than at the surface of the earth. (Rec. p. 25).

Claims 1 and 3 of the Doherty application define the invention as follows:

> "1. A method of obtaining oil from oil fields comprising forcing a liquefied mixture of butane and propane saturated with hydrocarbon gas into an oil stratum, and recovering oil from the stratum at a point remote from the point of introduction of the mixture into the stratum."
>
> "3. A method of obtaining oil from oil fields comprising forcing a liquefied mixture of butane and propane saturated with **hydrocarbon gas under** high pressure into an oil stratum, and recovering oil from the stratum at a point of relatively low pressure."

Doherty's Improvement on Wright.

Doherty's **gas-saturated liquid propane-butane** is a peculiarly effective oil recovery medium as compared to Wright's "gasolene". Wright's "Gasolene" is not efficient; goes into solution in and thins the oil, and stays in solution in the oil as it exits from the recovery wells "D". Unliquefied gas introduced by Wright does not go into solution in the oil to any marked extent, but may build up a gas pressure drive to push the oil toward the recovery well, as in prior practice. Wright's "gasolene" represents a very small percentage by volume of the gas entering the top of well "J" of Wright, the amount of recoverable gasolene in natural gas being normally less than one gallon for each thousand cubic feet of gas. (Rec. p. 30.)

Doherty's gas-saturated liquid propane-butane is in substantially 100 per cent liquid state as it reaches the bottom of the inlet well. It is completely soluble in the oil and therefore very materially reduces the viscosity of the oil, as explained by Beecher & Parkhurst's article—Exhibit F (Rec. pp. 58-65). The work described in Exhibit F was carried out under Appellant's direction (Rec. p. 22) and has been widely recognized as authoritative. For instance, in Dr. J. B. Umpleby's article published in "Mining & Metallurgy", March, 1932, referred to by Beecher (Rec. p. 20), the results outlined in Exhibit F are commented on as follows:

> "The most noteworthy later advance in knowledge came in 1926, when Beecher and Parkhurst published their paper on "Effect of Dissolved Gas upon the Viscosity and Surface Tension of Oil". This paper added to the old idea of an expelling force, the concept of a motivating agent that actually changes the physical characteristics of the oil and facilitates its movement through the pore spaces of the reservoir rock."

Doherty's oil recovery medium is a very powerful solvent for dissolving the oil films adhering to the sand particles, since by breaking down the capillary adhesion affinities between the oil and sand much larger volumes of oil are recoverable, as explained by Uren's article Exhibits D and E.

Another very important distinction between Doherty's reagent and Wright's "gasolene" is that by reason of its normally gaseous composition Doherty's reagent goes out of solution in the oil at a point of reduced pressure adjacent the inlet of the recovery well, and thereby supplies sufficient motivating energy to cause rapid flow of oil to and out of the recovery well (Rec. pp. 23, 28). Doherty's gas saturated propane-butane medium in going out of solution in the oil at points of reduced pressure supplies energy for moving the oil in a manner analogous in principle to that by which carbon dioxide escaping from carbonated beverage can carry with it a substantial portion of the contents of an uncapped bottle. (Rec. pp. 21, 39.) Doherty's reagent separates from the oil and leaves the recovery well in a gaseous state, as distinguished from Wright's liquid "gasolene" which remains in solution in the oil. Wright's "gasolene" thins the oil, but of itself supplies no energy for moving the oil. Any energy for moving the oil to the recovery well of the Wright patent must come from the driving effect of natural gas introduced as a gas under pressure into the oil strata through the well J.

New and Advantageous Features of the Doherty Process.

The Doherty process is not simply an obvious modification of that disclosed in the Wright patent. It is true that the propane C_3H_8 and butane C_4H_{10} employed by Doherty are related chemically to the "gasolene" employed by Wright. Doherty's reagent, however, differs materially from Wright's in its physical properties and in the way in which it functions in promoting removal of oil from the oil sands. Doherty's reagent is much more potent than Wright's reagent for lowering the viscosity and surface tension of the oil in the sand and for dissolving the oil films and liberating the oil held by capillarity in the sand pores. Doherty's reagent, being a liquid gas which is itself gas saturated, is much more soluble in petroleum than gasolene. Wright's gasolene, being a liquid at normal temperature and pressure, when once dissolved in the oil, stays in solution while the oil is removed from the sand. Doherty's reagent, being a gas at normal temperature and pressure, goes out of solution in the oil and resumes its gaseous state before the oil is removed from the well, and thereby supplies the energy necessary to flow the oil through the sand and out of the well. (Rec. pp. 22, 28.)

Mr. Beecher has estimated (Rec. p. 32) that the **Doherty process** would probably **increase production 400 to 500** per cent **as compared to** a maximum optimum **increase by** application of the **Wright** patent, of 100 per cent. Mr. Beecher has stated that liquefied propane-butane has proven successful recently in the Burbank field in Oklahoma for increasing oil recovery, and that it is the general consensus of opinion of production engineers consulted on this point that saturation of the propane-butane with gas in accordance with the Doherty invention would have greatly increased the recoveries obtained in this Burbank field test (Rec. pp. 26-27).

The curves shown in the article by Frolich **et al.**, comprising Appellant's Exhibit J (Rec. p. 80) corroborate Mr. Doherty's prior conception with respect to the selective solubility of gases such as methane in liquid propane-butane as compared with their solubility in gasoline. In other words liquid propane and butane is a much more efficient medium than is gasoline for introducing concentrated volumes of gaseous energy into solution in an underground oil body. Bureau of Mines Bulletin R. I. 3035, published by Chalmers **et al.** (Appellant's Exhibit H. Rec. pp. 66-72) gives data corroborating Mr. Doherty's conception that gas-saturated propane is a much more effective medium than dry natural gas for use in liberating oil from oil sands. Tables 5 and 6 of this exhibit emphasize clearly that propane even in the gaseous state and unsaturated by gas, is more than three times as efficient as an equal volume of dry natural gas when used for the removal of oil from sand. A liquefied propane-butane saturated with gas is much more efficient than gaseous propane for effecting oil removal from sand because, as explained by Mr. Beecher (Rec. p. 28), a gaseous hydrocarbon will not separate substantial quantities of oil from sand, whereas a gas-saturated liquid propane is probably the most efficient solvent available for recovering oil from sand. As explained by Mr. Beecher (Rec. p. 24) the curves of appellant's Exhibit M show that a solution of 10 per cent gasoline in an oil reduces its viscosity 6 per cent, ten per cent butane reduces the viscosity of the oil 47½ per cent, and 10 per cent propane reduces the viscosity 55 per cent. Likewise Lindsley in his preliminary Bureau of Mines article (Appellant's Exhibit I, Rec. p. 73-79) gives data showing that propane is much more soluble in oil than heavier gasoline hydrocarbons and accordingly is a much more efficient medium than gasoline for use in recovering oil from underground oil sands.

According to the Doherty process, energy in a highly concentrated form is introduced into solution in the oil in the underground oil body, the relative concentration of the energy thus introduced being indicated by comparison of the relative volumes of liquid and gaseous propane (one volume of liquid propane equals 35.48 volumes of gaseous propane at 60°F.). It must further be recognized that each volume of liquid propane employed in accordance with the Doherty invention is saturated with gas or, in other words, has many times its volume of methane and ethane gas in solution. The importance of effecting rapid rate of solution of gas in oil is explained in the article by Lacey, which is in evidence as Appellant's Exhibit K (Rec. pp. 81-84).

Because of the normally gaseous character of the Doherty energizing medium it is easily separated from the recovered oil at the top of the well for reuse after liquefaction and gas saturation. For this reason, and because the propane-butane used is at the present time a byproduct of the natural gas gasoline recovery industry having small value, the Doherty process has the additional advantageous feature of being inexpensive and therefore practical in application.

Evidence of Invention in Doherty Process.

The statutes and decisions give many tests for invention, such tests taking into consideration as evidence of invention not only novelty and utility, but also the difficulty and importance of the problem solved by the invention, the degree of interest of the art in the solution of the problem solved by the inventor, and the long elapsed time between the date of applicant's discovery and that of the best prior art reference. One of the most important tests for invention is expressed in the decision of O'Rourke vs. McMullen, 160 Fed. 938, as follows:

> "The principal question in such cases is: Has the patentee added anything of value to the sum of human knowledge, has he made the world's work easier, cheaper and safer; would the return to the prior art be a retrogression? When the Court has answered this question or these questions in the affirmative, the effort should be to give the inventor a just reward for the contribution he has made. The effort should of course be in proportion as the contribution is valuable. * * * The keynote of all the decisions is the extent of the benefit conferred upon mankind."

The great potency of the gas-saturated liquid propane-butane reagent employed by Doherty as compared to gas or gasoline is not simply the result of a change in degree of character of the two reagents because, as explained above, the Doherty reagent has characteristics such as gas saturation, quick solution in oil, as well as quick separation from oil at outlet well temperatures and pressures, which properties are not possessed by the gasoline described by Wright. Even if there were basis for considering that the Doherty invention differed from Wright only in degree, it is still apparent that a difference in degree oftentimes is sufficient to mark a meritorious invention. Thus the adjudicated validity of the famous Edison Incandescent Lamp Patent rests on the finding of the court in Edison Electric Co. vs. U. S. Electric Lighting Co., 52 F. R. 300, 1892, that Edison's use of a carbon filament 1/64th of an inch in diameter or less, in place of the prior art carbon wires of Sawyer and Mann, which were only 1/32th of an inch in diameter or more, represented invention and greatly increased the life and efficiency of the resultant lamp, which lies at the foundation of the incandescent electric lighting of the world. (See Walker on "The Law of Patents," 6th Ed. V. 1, p. 83.)

The fact that the problem of securing more oil than the 25-30% recoverable by present methods of production is the most important confronting the oil industry today, and has occupied for many years the attention of many hundreds of capable engineers and inventors, coupled with the fact that twenty years have elapsed since the filing date of the Wright patent reference, is further persuasive evidence of the presence of invention in this Doherty application. (Mantle Lamp Co. of America vs. Geo. H. Bowman Co. (C. C. A. 6) 11 U. S. Pat. Q. 127.)

As pointed out by Beecher in his testimony (Rec. pp. 31, 35, 36), there is a very close analogy between the problem to which the Doherty invention is directed, and the problem of removal of resins and terpenes from cellular wood, which is solved by the patent recently granted to Little No. 1,762,785 (Rec. pp. 85-93) (the file history of which is in evidence as Plaintiff's Exhibit N). The file of the Little patent contains copies, and the Patent Examiner's discussion, of numerous prior art references (Rec. pp. 94-115) cited against the Little patent disclosing the use of gasoline or petroleum ether and naphtha, for effecting removal of resins and terpenes from wood. (Clope, Rec. p. 95, line 46 shows naphtha; Walker, Rec. p. 98, line 44 mentions gasolene and naphtha; Frankforter, Rec. p. 104 suggests petroleum ether; Ogilvy, Rec. p. 109, line 71 suggests petroleum naphtha.) The Patent Examiner was persuaded to grant to Little a patent containing claims such as 3 and 4 (Rec. p. 92) directed broadly to the use of liquid butane and propane in place of the prior art use of gasoline and naphtha for effecting such extraction. The analogy between these two cases clearly indicates that the Patent Office has been inconsistent in its ruling on invention with respect to the Doherty application, because as a matter of fact, the Doherty invention differs from that of the Wright patent reference very much more clearly than does the invention of Little differ from the prior art disclosures cited in the file of the Little patent.

The Examiner's assumption that any person skilled in the art could adapt and modify the inoperative brine cooling process of the Wright patent so as to produce an operative process meeting the definition of the Doherty specification and claims, is a form of argument too often encountered. The answer thereto has been given by the Courts in many decisions, as for example that rendered by the D. C. Court of Appeals in Ex parte Henry, 55 App. D. C. 396,—conforming to the doctrine laid down by the U. S. Supreme Court in the case of Carnegie Steel Co. vs. Cambria Iron Co., 185 U. S. 403—to the effect that:

> "After a problem has been solved, its former difficulties are not so apparent and it is not hard to find those persons who confidently assert that their failure to solve the problem is due solely to the fact that it has not received their attention. The object of the Patent Law is to reward those who do successfully give these problems their attention, and who make real contributions to the useful arts."

Proposed Findings of Fact.

The court is urged to consider the following proposed findings of fact as a basis for a reversal of the Supreme Court's decree from which this appeal was taken:

1. Doherty's application discloses a method of recovering oil from a partially depleted oil bearing strata consisting of forcing a previously liquefied mixture of butane and propane saturated with hydrocarbon gas downwardly through an inlet well into the oil bearing strata, where it dissolves in the oil, thereby materially reducing its viscosity, washing the oil films free from the cellular sand pores, and by going out of solution in the oil adjacent the outlet well furnishes motivating energy for carrying the oil to and out through the outlet well.

2. The hydrocarbons utilized by Doherty are gaseous at normal temperature and pressure. Doherty liquefies the butane and propane and saturates the thus liquefied propane and butane with gaseous methane and ethane. All of these gaseous hydrocarbons are present in substantial amounts in natural gas, but not in Wright's "gasolene." Being normally gaseous, these hydrocarbons go out of solution in the underground oil body adjacent the outlet well and supply the energy for moving the oil, in a manner similar to that by which CO_2 gas escaping from beer can carry with it a substantial portion of the contents of an uncapped bottle.

3. The patent to Wright, No. 1,101,605 discloses a method of recovering oil by forcing hot gaseous hydrocarbons (natural gas) under pressure into the top of a well and downwardly therethrough to the oil-bearing rock, the oil and gases in liquid form being recovered

through another well. Prior to Wright it was old to introduce gas under pressure to "drive" the oil. Wright proposes (Rec. p. 119, l. 26-35) to liquefy **in the well** certain of the hydrocarbons introduced by thermal circulation of a cooling brine in the inlet well casing. Wright employs the term "gasolene" in referring to the gaseous hydrocarbons introduced through the inlet well (Rec. p. 118, l. 37, 75, and p. 119, l. 40). Wright definitely discloses that his "Gasolene" is a normally liquid hydrocarbon which **remains in solution in the oil** while the oil is removed through the outlet well (Rec. p. 119, l. 40).

4. The brine cooling system disclosed by Wright is practically inoperative for liquefying normally gaseous hydrocarbons such as propane and butane, or for saturating any liquid hydrocarbon with gas.

5. In granting the Little patent No. 1,762,785 (see claims 3 and 4) Appellee recognized the presence of patentable invention in Little's solution of a problem closely analogous to that faced by applicant, by the employment of liquid butane and propane for washing resins and terpenes from cellular wood, where the prior use of gasoline and naphtha for the same purpose was known.

6. Wright does not disclose or teach Doherty's idea of employing a reagent to be introduced into a well and consisting essentially of **liquid** propane and butane saturated with methane and ethane, for increasing the recovery of oil from underground sands through wells.

Proposed Conclusions of Law.

1. The Doherty patent application distinguishes in terms and patentably from the prior art adduced by appellee.

2. The Wright patent of 1914 having disclosed a practically inoperative process for liquefying gaseous hydrocarbons, cannot be interpreted as teaching plaintiff's novel and useful process directed to solution of this important problem of recovering oil left in the ground by present known methods of recovery.

3. Plaintiff is entitled to the decree asked by the Bill of Complaint.

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COURT OF APPEALS
DISTRICT OF COLUMBIA
FILED

FEB 1 - 1933

Henry W. Hodges
CLERK

No. 5762

In the Court of Appeals of the District of Columbia

Henry L. Doherty, appellant

v.

Thomas E. Robertson, Commissioner of Patents
appellee

BRIEF FOR THE COMMISSIONER OF PATENTS

T. A. HOSTETLER,
Solicitor United States Patent Office.

In the Court of Appeals of the District of Columbia

No. 5762

Henry L. Doherty, appellant
v.
Thomas E. Robertson, Commissioner of Patents
appellee

BRIEF FOR THE COMMISSIONER OF PATENTS

STATEMENT

This is an appeal from the final decree dismissing appellant's Bill of Complaint filed in the Supreme Court of the District of Columbia under Section 4915 R. S.

The subject matter involved in this suit is a process for operating upon an oil field having a plurality of depleted or partially depleted oil wells in which hydrocarbon gas is forced into one of the wells and into the subterranean space under pressure to entrain oil and carry it out of one of the other wells that may be left open.

The patent to Wright, 1101605, June 30, 1914, discloses this process which is diagrammatically illustrated in Fig. 1 (R. 116) and clearly described in the Wright specification. Appellant's application has no drawing and many of the details of the process are lacking in the specification. Appellant contends that his process is an improvement over the Wright process in the particular kind of gas he uses in his process.

THE WRIGHT PATENT

The Wright patent discloses two methods, one of which is in substance the method disclosed and claimed by appellant, which method is illustrated in Fig. 1 where 3 indicates a reservoir or closed-top steel storage tank of large capacity for oil and gas. Gas may be drawn from this reservoir 3 through pipe 8 (R. 118, line 95) to the gas compressing pump at 6 and forced under compression into the adjacent well J. The gas in the top of the reservoir is rich in propane and butane, as is well known by those skilled in this art.

In the Handbook of Petroleum, Asphalt, and Natural Gas, by Roy Cross, published as Bulletin No. 24 (1928) by the Kansas City Testing Laboratory, Kansas City, Mo., on page 147, is given an analysis of vapors from storage tanks of crude oil as follows:

	Per cent
Methane+Nitrogen	8.1
Ethane	13.9
Carbon Dioxide	1.0
Propane	29.4
Butane	41.7
Pentane, etc	5.9

As further shown in Fig. 1 and described on page 1 of the Wright patent, lines 90 to 95, gas may be taken from any source by the pipe 7 to the compressing pump at 6 and forced into the well J.

WRIGHT AND DOHERTY PROCESSES COMPARED

Both operate in the same field upon a plurality of wells more or less depleted. Both force hydrocarbons into the wells under compression. Wright describes and illustrates how he does it but Doherty merely makes general statements. When Wright utilizes the gas from the storage tank 3 he has a gas rich in propane and butane, which of course is compressed by the compression pumps at 6. In the wells and the underground space between the wells this compressed propane and butane is mingled and compressed with other and lighter hydrocarbons which results in the same product as that used in the Doherty process.

The enormous quantity of gas required to carry into effect the process disclosed by appellant and by Wright becomes apparent when we consider that the wells may be as much as a mile or more apart, as stated by Wright at the end of page 1. (R. 118.) It is therefore apparent that carefully measured quantities of ingredients in the gas used would not be practical. This also appears from the specifications of both parties. Wright uses the gas from the dome of the storage tanks, which gas is rich in propane and butane, or gas which "rises in some wells from the oil contained in the oil-bearing rock" (line 24).

ARGUMENT

Appellant critizes the method by which Wright cools the gas that he injects into the well. Before we discuss that question let us ask how Doherty cools the gas. The answer must be found in his specification (R. 38) as filed, and can not be supplemented by new matter injected into his application.

Appellant's witness, on cross-examination (R. 33), admitted that the Doherty application contains no explanation of the manner in which the liquid propane and butane was cooled, the application simply explaining that propane and butane was liquefied and saturated with natural gas.

Obviously under those conditions appellant is not in a position to urge that the Wright brine cooling system is not operative. Either appellant's application must be held incomplete as not disclosing how the gas is cooled or else cooling methods must be regarded to be so well known as to require no description. Applying the same rule to the Wright patent, a mere diagrammatic outline to indicate that cooling with brine is contemplated in his method would be sufficient without any explanation as to details.

Appellant at the bottom of page 6 of his brief says:

> Practical application of the Doherty process requires that the propane and butane

> be liquefied by very efficient refrigeration before being introduced to the injection well.

What is the efficient refrigeration? None whatever is described in the specification. Compression only seems to be relied upon. Wright has both compression and cooling for liquefying the gas.

In appellant's brief (page 7) under the section entitled "Doherty's Improvement on Wright," appellant is evidently not following the teaching of the Wright patent. Reference is made to "Unliquefied gas introduced by Wright." Wright distinctly says on page 1, line 74, "The gas in well B becomes liquefied by high pressure and by cooling means." (Doherty relies upon pressure alone.) As a gas rich in propane and butane appellant appears to overlook Wright's alternative method of utilizing the gas in the top of the storage tank, which as stated is rich in propane and butane.

A mere reading of the opening paragraphs of the Wright specification is convincing that where he uses the word "gas" he means "gas" and not "gasolene" ~~are~~ as argued by appellant.

It is submitted that appellant in his application teaches nothing patentable over what is found in the Wright patent. Wright's patent has expired. Not only is Wright's exact disclosure free to the public but also such changes as would naturally suggest themselves to those skilled in that art in the oil fields. Wright includes both extremes, i. e., gas on one hand and a mixture rich in propane and butane on the other. Obviously the public should not be deprived of the use of the intermediate mixtures in such proportions as may be found to be most efficient, or the gas that is available in that field irrespective of the proportions of the first five members of the marsh gas (paraffin) series that it may contain.

THE CLAIMS

Claims 1 to 11 for which appellant contends appear in the Examiner's Statement on pages 43 to 45 of the Record.

Claims 1 to 4 call for "a liquefied mixture of butane and propane." Since the gas in the dome of oil storage tanks consists largely of butane and propane, and as Wright uses the gas from the storage tank and forces it into the wells by means of the compressing pumps at 6 it not only becomes liquefied but is also mixed with other hydrocarbon gas inherently in the well or pumped into the well from the pipe 7. (R. 116.) This compressed mixture passing through the oil stratum absorbs or entrains the oil and carries it to the surface through any adjoining well that may be left open for that purpose. It is submitted that claims 1, 2, 3, and 4 define nothing patentable over the Wright disclosure.

Claims 5, 6, and 7, and 10 define the marsh gas (paraffin) member as having "less than six carbon atoms" which means that it is one or more of the following: methane, ethane, propane, butane, or pentane, which have, 1, 2, 3, 4, and 5 carbon atoms respectively. (R. 45.) Inasmuch as Wright uses the gas mixture from the dome of the storage tank and as that gas contains each of these members of the paraffin series, it is submitted that these claims define nothing patentable over Wright.

In claim 8 the mixture is defined by the relative gravity, viscosity, and surface tension. It is however the same mixture defined in the other claims in different or more specific terms.

Claim 9 specifies the relative volume of gas and liquid. The compressibility of this gas is recognized by Wright in the statement that:

> One million feet of gas can be stored under pressure in the space of 50 to 100 barrels of petroleum.

It is thus apparent that in the Wright process as described and practiced the proportions specified in claim 9 would result. Even if it were less (which is not admitted) it would be merely a matter of degree of a character that would not constitute a patentable distinction.

Claim 11 emphasizes the face that the "oil in the strata is subjected to the motivating action of both liquid and gas." It is perfectly proper to assume that the propane-butane mixture that Wright obtains from the dome of the storage tank for compression in the well will act on the oil no different than does the propane-butane mixture that appellant obtains from (not stated in the specification).

Furthermore the gas and liquid mixture that Wright forces into the well and that carries the oil into and out of the exit well certainly has a motivating action on the oil.

APPELLANT'S PROPOSED FINDINGS

Appellant's brief submits proposed findings of fact and proposed conclusions of law.

It is submitted that the Findings of Fact and the Conclusions of Law (R. 8–9) adopted by the Court below should not be disturbed.

It is further submitted that the findings proposed by appellant form no basis for a reversal of the decree herein. To specify in detail the objections to the proposed findings would in effect be to rewrite the argument in this brief. A few only will be mentioned.

1. The intimation that Wright operates with gasoline or with hot gaseous hydrocarbons finds no valid support in the Wright specification. In lines 73 et seq. it is stated:

> The gas in well B becomes liquefied by high pressure and by cooling means * * *.

The criticism of the Wright cooling system can not well form a basis for reversal when appellant's specification discloses none at all and the cooling step is not mentioned in any of the claims. Even if the brine circulating system of Wright is not the most efficient, any mechanic could make the changes necessary to make it more efficient. At any rate, Wright shows some cooling means and that is more than appellant does. A mere reading of the disclosures of the Wright patent and the Doherty specification should be convincing that Wright teaches the process more fully than the Doherty specification does, particularly the compressing and cooling steps. The query is what becomes of the "previously liquefied mixture" when it is pumped into an empty earth-temperature well and the pressure that liquefied it is removed, and whether it returns to its gaseous state and remains in that state until the wells are filled to their capacity so liquefying pressure can again be applied.

CONCLUSION

It is respectfully submitted that the Court below should be affirmed.

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Solicitor for the Patent Office,
Attorney for Appellee.

January 26, 1933.

U. S. GOVERNMENT PRINTING OFFICE: 1933